Analysis of the Large Scale Centralized Hydrogen Production and the Hydrogen Demand from Fuel Cell Vehicles in Ontario

by

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A thesis

presented to the University of Waterloo

in fulfillment of the

thesis requirement for the degree of

Master of Applied Science

in

Chemical Engineering

Waterloo, Ontario, Canada, 2009

Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

The 'Hydrogen Economy' is a proposed system where hydrogen is produced from carbon dioxide free energy sources and is used as an alternative transportation fuel. The application of hydrogen on board fuel cell vehicles can significantly decrease air pollutants and greenhouse gases emission from the transportation sector. There must be significant transition of infrastructure in order to achieve the hydrogen economy with the investment required in both production and distribution infrastructure. This research focused on the projected demands for infrastructure transition of 'Hydrogen Economy' in Ontario, Canada. Three potential hydrogen demand and distribution system development scenarios were examined to estimate hydrogen fuel cell vehicle market penetration, as well as the associated hydrogen production and distribution. Demand of transportation hydrogen was estimated based on the type of hydrogen fuel cell vehicle. Upon the estimate of hydrogen demand from fuel cell vehicles in Ontario, the resulting costs of delivered hydrogen were investigated.

In the longer term hydrogen is expected to be produced by utilizing nuclear heat and a thermochemical production cycle. A brief survey of thermochemical hydrogen production cycles was presented with a focus on S-I cycle. Sequential optimization models were developed to explore the minimum utility energy consumption and the minimum number of heat exchangers. Finally an optimal heat exchanger network for S-I thermochemical cycle was defined by a mixed integer optimization model using GAMS.

Acknowledgements

I would like to express my gratitude and appreciation to my supervisors, Professor Michael Fowler and Ali Elkamel for their great guidance, encouragement and support. I am also grateful to the readers of the thesis, Dr. Evgueniy Entchev and Mazda Biglari for their valuable suggestions.

I would like to thank all my friends and colleagues at process control and simulation lab for their kindness and generosity.

Finally, I would like to thank my parents for their emotional support. Special thanks go to my wife, Haiyan Wang, for her love, support, patience, and understanding.

Dedication

To my baby, Michael Liu.

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Nomenclature

a_{FCV}	coefficient of logistic model
b	learning index
b_{FCV}	coefficient of logistic model
C	cumulative capacity
C_0	initial cumulative capacity
CabPrice	cost of a liquid hydrogen truck cab ($)
CompCap	cost of high pressure hydrogen compressors ($)
CompCool	base cooling water consumption of hydrogen compressors (gallon / kg H_2)
CompCost	base capital cost of hydrogen compressors ($/kW)
CompExp	size exponent of hydrogen compressors
ComPower	base power consumption of hydrogen compressors (kWh/ kg H_2)
CompSize	base size of hydrogen compressors (kW)
Cooling	cooling water consumption of high pressure hydrogen compressors (gallon/h)
$CP_{depreciation}$	unit depreciation of capital investment ($/kg H_2)
$CP_{electricity}$	unit cost of water electrolysis power consumption ($/kg H_2)
CpExp	pressure exponent of hydrogen compressors
$CP_{labor\ and\ related}$	unit cost of labor and related parts ($/kg H_2)
CP_{water}	unit cost of water consumption of electrolysis ($/kg H_2)
$CS_{cooling\ water}$	unit cost of cooling water consumption from compression ($/kg H_2)
$CS_{electricity}$	unit cost of energy consumption from compression ($/kg H_2)
$CS_{depreciation}$	unit depreciable hydrogen gas storage capital investment ($/kg H_2)
CW	heat absorbed by the cold utilities
D	hydrogen gas pipeline diameter (meter)
DewarExp	size exponent of hydrogen storage tanks
E_{compr}	power consumption of high pressure hydrogen compressors (kW)
$E_{consumption}$	electricity consumption of water electrolysis (kW)
$\boldsymbol{\varepsilon}_{conversion}$	conversion efficiency of water electrolysis process (%)
$\boldsymbol{\varepsilon}_{energy}$	energy efficiency of water electrolysis (%)

$F_{hydrogen}$	flow rate of hydrogen output (kg H_2/h)
H_{FCVs}	fuel economy of hydrogen fuel cell vehicles (kg H_2/km)
$H_{heating\ value}$	high heating value of hydrogen (kWh/kg H_2)
HT_{FCVs}	Ontario's hydrogen demand from H_2 FCVs each year (kg H_2/year)
HY_{FCVs}	average hydrogen demand of a hydrogen fuel cell vehicle each year (kg H_2/ FCV. year)
L	distance (km)
L_{cost}	labor cost (\$/kg H_2)
LiqCool	unit cooling water consumption of hydrogen liquefiers (gallon/kg H_2)
LiqCost	unit cost of liquefiers (USD, h/kg H_2)
LiqExp	size exponent of hydrogen liquefiers
LiqPower	unit power consumption of hydrogen liquefiers (kWh/kg H_2)
LiqSize	base size of hydrogen liquefiers (kg H_2/h)
LM	average Ontario's vehicles lifetime mileage (km)
LT	average Ontario's vehicles lifetime (year)
$M_{hydrogen}$	hydrogen molecular weight (kg H_2 /mol)
M_{water}	water molecular weight (kg H_2O/mol)
$N_{accumulation}$	accumulated number of H_2 FCVs sold from the 1st year to the year i (vehicle)
N_{FCV}	number of new H_2 FCVs sold each year in Ontario (vehicle)
N_i	number of H_2 FCVs running on road in the year i (vehicle)
$N_{new\ car\ sale}$	number of new vehicles sold each year in Ontario (vehicle)
$N_{operator}$	number of operators at a shift (operator/shift)
$N_{out\ of\ vehicle\ lifetime}$	total number of H_2 FCVs beyond vehicle lifetime (vehicle)
$N_{registered\ vehicles}$	number of Ontario's registered vehicles (vehicle)
$N_{unused\ car}$	total number of unused H_2 FCVs (vehicle)
P	operating pressure of hydrogen compressors (bar)
P_0	atmospheric pressure (bar)
P_1	base pressure of hydrogen compressor (bar)
P_{FCV}	H_2 FCVs market share (%)
Pr	progress ratio

$Q_{i,j,k}$	the heat transferred from hot stream i to cold stream j
$Q_{i,n,k}$	the heat transferred from hot stream i to cold utility n
QC	heat absorbed by cold streams
QH	heat supplied by hot streams
$QH_{i,k}$	the heat content of hot stream i at temperature interval k.
QS	heat supplied by hot utilities
$QS_{m,k}$	the heat content of hot utility m at temperature k
$QS_{m,j,k}$	the heat transferred from hot utility stream m to cold stream j at interval k
R_k	heat residual from temperature interval k
$RH_{i,k}$	the heat residual of hot stream i at temperature interval k
$RS_{i,k}$	the heat residual of hot utility m at temperature interval k
SC	unit cost with cumulative capacity C ($/ unit)
SC_0	Initial unit cost with initial cumulative capacity ($/ unit)
$S_{operator}$	wage of operators ($/ h. operator)
StorageCost	unit cost of liquid hydrogen storage ($/kg H_2)
StorageSize	base size of liquid hydrogen storage (kg H_2)
t	time (year)
t_0	the year of H_2 FCVs entering new vehicles market (year)
TankCap	cost of hydrogen storage tanks ($)
TankCost	base tank cost ($/kg H_2)
TankExp	size exponent of storage tanks
TankPress	base pressure of hydrogen storage tanks (bar)
TankSize	base tank size (kg H_2/tank)
TCP	total cost of electrolysis hydrogen generation ($/kg H_2)
TCS	total cost of gaseous hydrogen storage ($/kg H_2)
TD	average Ontario's vehicles travel distance (km/vehicle. year)
TD_{total}	total estimated travel distances of all vehicles in Ontario (km/year)
TPExp	pressure exponent of storage tanks

TrailerPrice	cost of a liquid hydrogen truck trailer ($)
TranspHours	time of liquid hydrogen transportation (h)
TruckCap	capital cost of a cryogenic tank truck ($)
StorageCap	cost of liquid hydrogen storage ($)
$U_{i,j}$	the upper limit of heat transferred between cold stream j and hot stream j at interval k
$U_{i,n}$	the upper limits of heat transferred from hot stream i to cold utility n
UnderPrice	cost of a liquid hydrogen truck undercarriage ($)
$US_{m,j}$	hot utility m to cold stream j
$W_{consumption}$	water consumption by water electrolysis (kg H_2O/h)

Chapter 1

Introduction

Hydrogen is a common element that holds the promises of a green energy future. Currently hydrogen is applied widely in the chemical industries as an important chemical intermediate. Hydrogen can be used to produce ammonia and other fertilizers. In the oil refinery industry, hydrogen is also a key chemical to the process of hydrocracking and hydrogenation. In the recent years, hydrogen has attracted a great attention due to concerns about the global warming and energy crisis. As a “green” energy carrier, hydrogen is regarded as a replacement of fossil oil in the transportation sectors and the application of hydrogen fuel cell vehicles can decrease greenhouse gases and air pollution emission considerably. This thesis was focused on the development of the ‘hydrogen economy’ in Ontario, specially the methods of hydrogen production and the costs of hydrogen production, storage and distribution.

In Chapter 2, a literature review of hydrogen production, hydrogen storage and distribution was conducted. The processes of the hydrogen production such as steam methane reforming, water electrolysis, high temperature electrolysis and thermochemical cycles were introduced. Storage and distribution of compressed hydrogen gas, cryogenic hydrogen liquid and metal hydride were studied as well. A brief introduction to the applications of fuel cells was made in the last section.

A detailed study of hydrogen demand, hydrogen production, storage and distribution was implemented in Chapter 3. Three scenarios were developed to estimate the development of Ontario’s hydrogen fuel cell vehicle market and hydrogen demand from fuel cell vehicles. With the projected demand, a hydrogen production analysis model was established to estimate the costs of hydrogen production, storage and distribution in Ontario. A sensitivity analysis was conducted to assess the impact of various factors on the hydrogen costs.

Chapter 4 was mainly focused on the thermochemical sulfur-iodine (S-I) cycle hydrogen production method. The reactions and the conceptual design of S-I cycle were introduced first, and based on the collected heat duty data, a series of sequential models were built to optimize the heat exchanger network of S-I cycle. Eventually, an optimized heat exchanger network was achieved by a mixed integer linear model.

In Chapter 5, general conclusions were drawn from the previous chapters and some recommendations were made for the future research.

Chapter 2

Literature Review

Hydrogen is abundant on the earth but there is no pure hydrogen in the natural world. Hydrogen always combines with other elements to form many common materials. As an element hydrogen mainly exists in water, fossil hydrocarbons, coal, petroleum, natural gas, oil shale, biological materials, carbohydrates, protein, cellulose, and minerals. As such hydrogen is not a primary energy resource, but in the future hydrogen may become a replacement of fossil oil, especially in the transportation sectors as a hydrogen onboard vehicle fuel.

2.1 Definition of Hydrogen Economy

Hydrogen economy is a hypothetical future economy in which hydrogen is produced, stored and delivered for the purpose of being a replacement of fossil fuels in the transportation sectors. With the onboard hydrogen fuel cell technologies, zero emission can be achieved from the vehicle operation itself. However, currently hydrogen is still produced as a chemical feedstock and intermediate instead of a fuel of hydrogen fuel cell vehicles. Approximate nine million tons of hydrogen are consumed annually in chemical production, petroleum refinery, metal treating, and electrical applications in the United States [1], but in the future hydrogen will be regarded as a ‘clean energy carrier’ to replace the role of fossil oil in the transportation sectors as the fuel cell technologies become fully commercialized.

2.2 Hydrogen Economy Structure

A ‘hydrogen economy’ is composed of five segments: hydrogen production, storage, delivery, conversion and end-use applications. Fossil fuels, electricity and nuclear energy can be utilized to generate hydrogen through chemical, electrolytic, thermal and photolytic processes. After that, hydrogen is stored either as a liquid or gas and is delivered by pipelines, trucks, trains, and barges.

The interconversion of hydrogen and electricity enables to take the full advantage of off-peak electricity price to store or release energy, but eventually hydrogen will work as an energy carrier to fuel H_2 FCVs (hydrogen fuel cell vehicles) or the stationary and portable power generation facilities.

2.3 Benefits of Hydrogen Economy

Energy security, urban air pollution, air pollution health effects and the global warming are the major factors to promote the hydrogen economy.

Currently, most of industrial countries' economies become more dependent on fossil oil. From 1990 to 2007, the energy demand in Canada increased by 26% and about 30% of the total energy was consumed by the transportation sectors [2]. In the USA over two-third of the total oil is consumed by the transportation everyday [3]. Globally, the energy demands in developing countries such as China and India are also growing rapidly. With regard to concerns about the global energy crisis, diversifying energy resources and exploring an alternative energy become a must for sustaining the global economy. Considering that a hydrogen fuel cell vehicle consumes 50% of fuels less than a conventional vehicle with a gasoline internal combustion engine [3], hydrogen can be a solution to the global energy crisis. Furthermore, hydrogen can be generated from a variety of energy sources like coal, nuclear, wind and solar energy, hydrogen thus offers the promise of energy security through great production and uses of domestic energy sources. Eventually when the world runs out of fossil fuels especially oil and at the time society will be forced to transition to alternative fuels such as hydrogen. Thus, the transition to alternative fuels is unavoidable

Another critical benefit from the use of hydrogen is the ability of hydrogen as an electrical energy storage medium. Renewable energy sources such as wind and solar are intermittent in nature, and thus require energy storage for fuel integration into the electricity distribution system. The

production of hydrogen provides the energy storage medium. During an off-peak electricity demand period, electricity generated by wind and solar can be utilized to produce hydrogen and be stored as a liquid or a gas while in a peak demand period the energy of stored hydrogen can be released and exported to electrical grid. For electrically powered, zero emission vehicles, batteries are limited in range, do not allow for rapid refueling and are costly; onboard use of hydrogen allows for zero emission vehicles with extended range and rapid refueling. The conversion of electricity to hydrogen has approximately 80% efficiency and electrical energy can be stored in hydrogen and ready to be released for peak electricity demand. The economics of production, storage and the utilization of hydrogen based electrolysis become quite relevant in the context of competitive electricity markets, given the significant price differences between peak and low price periods that may or may not necessarily coincide with peak and low demand periods. The benefits of hydrogen are even greater considering the applications with carbon dioxide free generation resources such as nuclear energy as well as the costs of environmental pollution and the carbon credits. Additionally, since the traditional generations plants are most efficient when operation at rated load levels, and considering congestion problems in the electricity transmission system during the normal operation of a power grid, the use of hydrogen as an energy carrier to increase the efficiency and reliability of the grid is certainly attractive, especially with increased integration of intermittent renewable energy such as wind and solar [4-11].

Variable operation of electrolyzers can provide auxiliary electrical services such as the voltage regulation that the generated hydrogen can be used to generate electricity during peak demand periods or for the transportation sectors. Ontario is increasing the supply of wind power in Ontario, and thus the use of surplus electricity from off-peak demand periods or the periods when wind production exceeds demand or transmission capacity can be utilized to generate hydrogen,

which can be converted into the electricity during peak demand periods.

Most importantly the application of hydrogen powered fuel cell vehicles can also improve urban air quality and human health. According to Health Canada, air urban pollutants such as carbon monoxide, nitrogen oxides, sulfur oxides, particulate matter and ground-level ozone are the precursors to the generation of photochemical 'smog' in the urban environment [12]. Vehicles use in the urban environment is a big contributor to health effects. Such air pollutants affect the health of human respiratory and cardiovascular systems. The air pollutants like ozone, metals and free radicals can damage lung tissue cells and these toxic chemicals can also penetrate human circulatory system to harm heart and nerves. Air pollutants can cause structural damages to the organs through interacting with organ tissues. Figure 2.1 shows health effects of air pollution. The bottom part represents the mildest and most common health effects of air pollutions while the top part stands for the most severe but rarest effects. A study conducted by Environment Canada showed that the six–million dollar fuel improvement programs ultimately avoided 24 billion dollars health care cost during a 24-year period [13], whereas the applications of zero emission hydrogen fuel cell technologies can gain much more benefits than that.

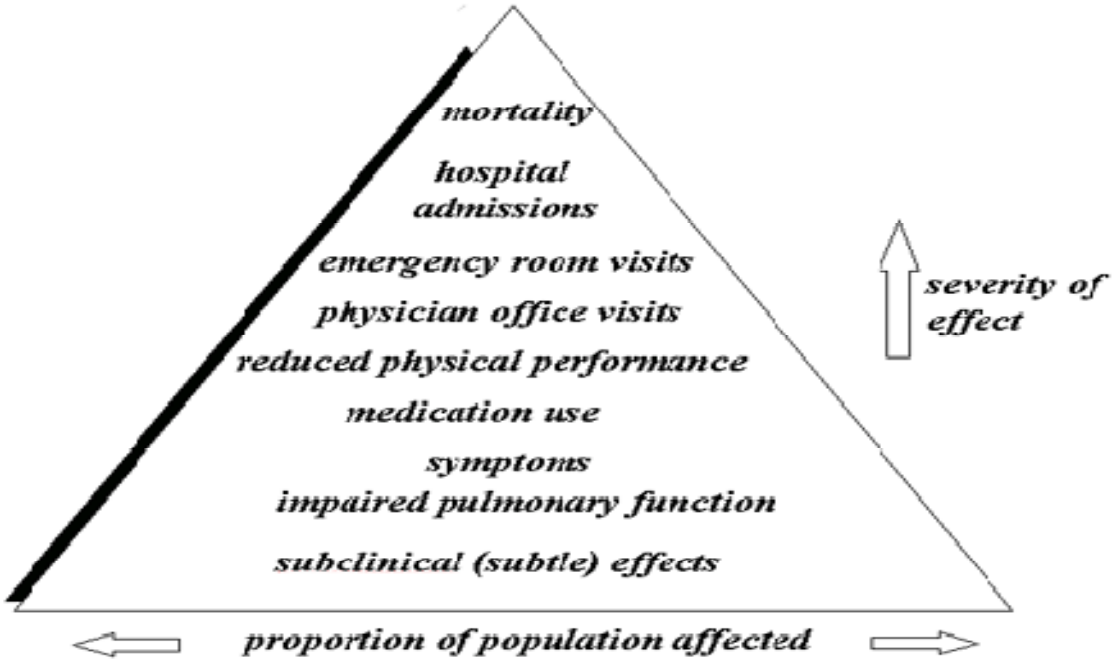


Figure 2.1: Health Effects of Air Pollution [13]

Climate change is another big concern. Automobile fuel combustions emit not only air pollutants but also enormous amount of greenhouse gases. The greenhouse gases such as water vapour, carbon dioxide, methane, nitrous oxide, ozone and other trace gases in the atmosphere absorb and emit the thermal radiations from surface of the earth to keep energy balance between atmosphere, space, oceans and lands. A change of greenhouse gas concentration may alter the average temperature of the earth. Some evidences showed that the human activities had impacted the greenhouse gas concentrations and the global climate was altered to some extents [14]. In Canada, the total greenhouse gas emissions rose by 25% from 1990 to 2005, and 33% of the emissions came from the transportation [15]. In the USA, the total greenhouse gas emission increased by 14.7% from 1990 to 2006 while the transportation accounted for about 30% of the total emissions. The zero emission hydrogen fuel cell technology is a solution to the global warming, and with the wide application of onboard fuel cells the transportation emissions can be reduced radically.

2.4 Options for Hydrogen Production

A variety of energy resources such as fossil fuels, nuclear, solar, wind, hydro-electric and geothermal energy can be utilized to generate hydrogen, thus with different energy resources, various pathways can be applied to generate hydrogen. Note that this variety of energy sources and production pathways will contribute significantly to the nation's energy security and sovereignty.

With respect to production capacities and locations, hydrogen production can also be categorized into 'distributed' or 'centralized' production. Distributed production facilities are smaller in scale and closer to the consumers. As such distributed generations can meet the demand from small fleets of hydrogen powered fuel cell vehicles during the transition period to a hydrogen economy and once the market expands, the hydrogen production will be scaled up and 'centralized' to take advantage of economies of scale as well as the higher efficiency from larger scale production and to meet the greater amount of hydrogen demand.

Various processes such as methane steam reforming, water electrolysis, high temperature electrolysis, and thermochemical cycles are available to produce hydrogen as well. Currently methane steam reforming is the most common way and about 95% of hydrogen products are generated through this method. The following sections will discuss these hydrogen production processes.

2.5 Hydrogen Production Process

2.5.1 Steam Reforming of Natural Gas

The ratio of hydrogen and carbon varies in the different types of hydrocarbons. As shown in Table 2.1, methane is the best chemical compound to generate hydrogen [16]

Table 2.1: Ratios of Hydrogen and Carbon in Hydrocarbons [17]

	Atomic H/C Ratio
Methane (CH_4)	4
Petroleum (heavy fuel oil)	1.5-1.6
Oil shale	1.6
Coal	0.72-0.92

With the current moderate natural gas price, steam reforming of natural gas (SMR) is the most economical and efficient method to generate hydrogen for large scale production, although currently economical natural gas price is expected to increase as reserves will be depleted over the next decades and the production method contributes to climate change with the carbon dioxide emissions. Generally, natural gas steam reforming process consists of two steps, reformation of natural gas reaction and shift reaction.

The reactions are shown as follows,

Reforming reaction: $CH_4 + H_2O \rightarrow CO + 3H_2$

Shift reaction: $CO + H_2O \rightarrow CO_2 + H_2$

Net reaction: $CH_4 + 2H_2O + Heat \rightarrow CO_2 + 4H_2$

Hydrogen is generated from water, methane in two reactions and carbon dioxide is produced as a by-product. As illustrated in Figure 2.2, natural gas passes through the desulfurization unit to reduce catalytic sulfur compound level, and then is fed into the reformer to react with the superheated steam at 750-800°C [19].

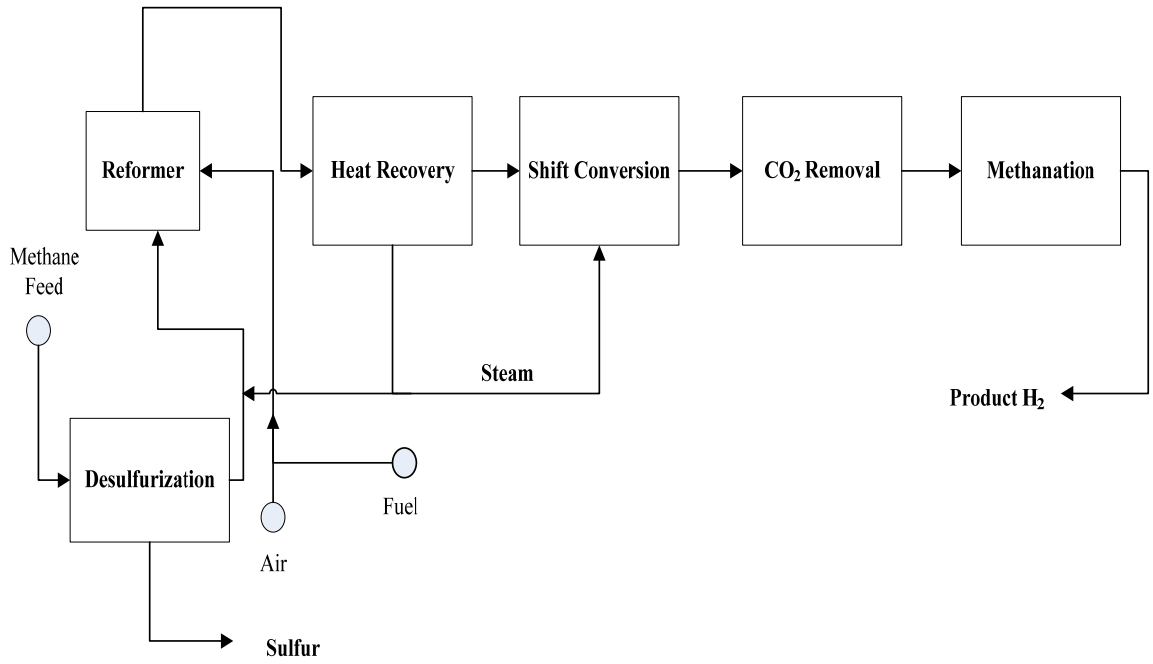


Figure 2.2: Simplified Flow Diagram of Steam-Methane Reforming Process [18]

The synthesis gas generated in the reformer is a mixture of hydrogen, monoxide, carbon dioxide and residual methane. The heat is recovered when synthesis gas passes through a series of heat exchangers, and the generated superheated steam is sent back to the reformer. In the shift reactor, carbon monoxide is converted into carbon dioxide over an iron oxide chromium oxide catalyst, and another part of hydrogen is released from water. The shift process consists of two stages, high temperature shift at 350°C and a low temperature shift at 190-210°C The shifted gas stream is then compressed and goes through carbon dioxide removal process. The major part of carbon dioxide is eliminated by the absorption system, a mono-ethanolamine and hot potassium carbonate system. At the next step, the residual trace amount of carbon oxides is removed by the process of methanation, shown as follows,

$CO + 3\ H_2 \rightarrow CH_4 + H_2O$

$CO_2 + 4\ H_2 \rightarrow CH_4 + 2H_2O$

The further hydrogen purification process may be needed for fuel cell applications as the impurities in hydrogen may cause catalyst poisoning and membrane failures especially sulfur compounds and carbon monoxide. Note that production via natural gas steam reforming contributes to the production of carbon dioxide which is the key contributor to the global warming. Finally the costs associated with hydrogen production are currently closely related to the cost of natural gas. In the future the cost of natural gas is expected to increase dramatically, which will limit the natural gas steam reforming production. Nevertheless as the principal method of production, SMR must be considered in the discussion.

2.5.2 Partial Oxidation of Heavy Oil

The key process of partial oxidation of residual oil is gasification. There are mainly two fully commercialized gasification processes for large scale hydrogen production, Shell and Texaco Gasification processes. Figure 2.3 demonstrates the simplified flowchart of Texaco gasification process.

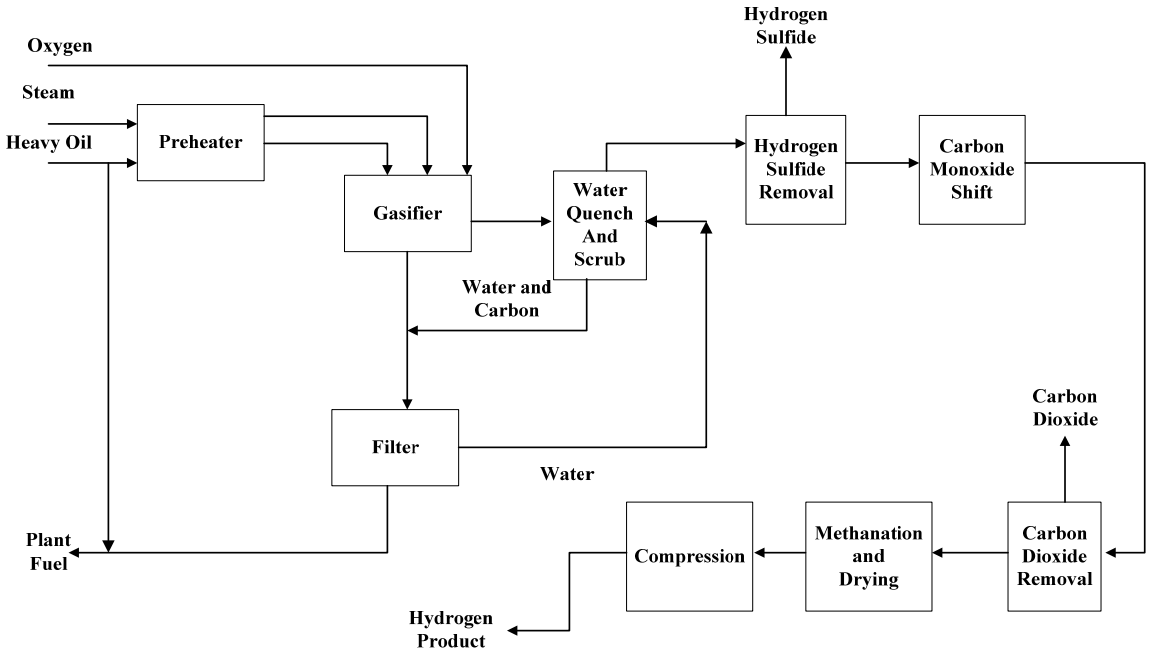


Figure 2.3: Texaco Partial Oxidation Process (heavy oil to hydrogen) [18]

The preheated steam and heavy oil are mixed with the specific ratio and are injected into the gasifier together with high purity oxygen. In the gasifier, the synthesis gas, a mixture of carbon monoxide, carbon dioxide and hydrogen is generated. The oil residue in the gasifier is removed by the filter and is sent back as a fuel of the preheater. The heat of gasification reaction is recovered to generate the internal steam in the process of quench and scrub. Since some amounts of sulfur exist in the heavy oil feed, raw gas in the gasifier contains sulfur contents, so the raw gas leaving the gasifier is firstly sent to remove sulfur contents and then goes through the gas shift, the carbon dioxide removal, and the methanation units to eliminate hydrogen sulfide carbon monoxide and carbon dioxide. Finally, the purified hydrogen gas is output as a product.

2.5.3 Coal Gasification

Hydrogen can be produced from coal. As demonstrated in figure 2.4, Coal reacts with oxygen and steam in the gasifier. The generated raw gas undergoes shift conversion, acid gas removal and methanation to produce hydrogen. This process is of less interest to this study as the wide scale application of coal gasification will have a major negative impact on the climate change, but other studies do consider this process with carbon capture and sequestration in the future [20-21].

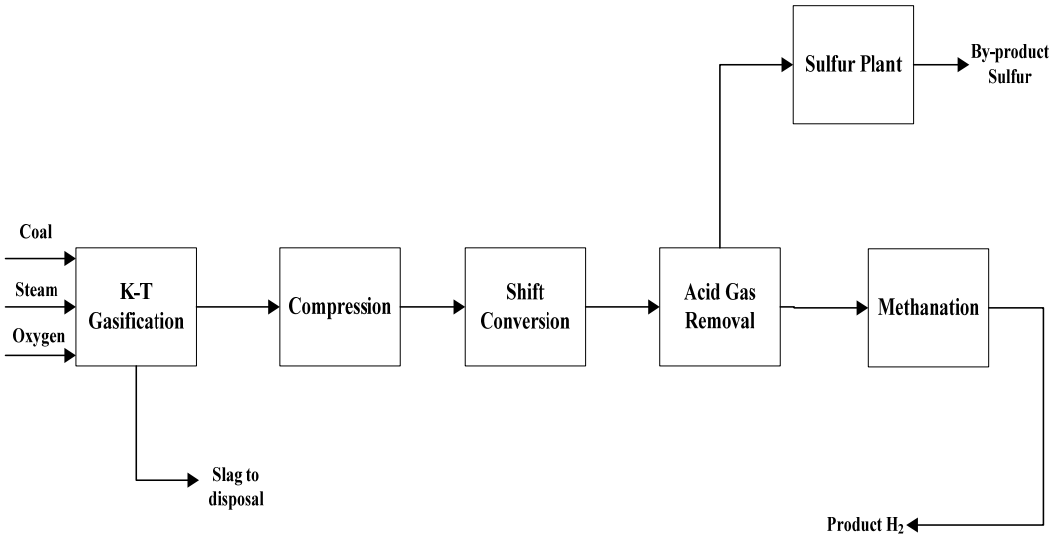


Figure 2.4: Simplified Koppers-Totzek Coal Gasification diagram [18]

2.5.4 Water Electrolysis

As displayed in Figure 2.5, direct electrical current splits water into hydrogen and oxygen. Water essentially dissociates into hydrogen and hydroxide ions, so when the direct current passes through water, hydrogen ions emigrate to the cathode while hydroxide ions accumulate at the anode, and then hydrogen ions receive electrons to generate hydrogen gas, whereas hydroxide ions release electrons to generate oxygen gas.

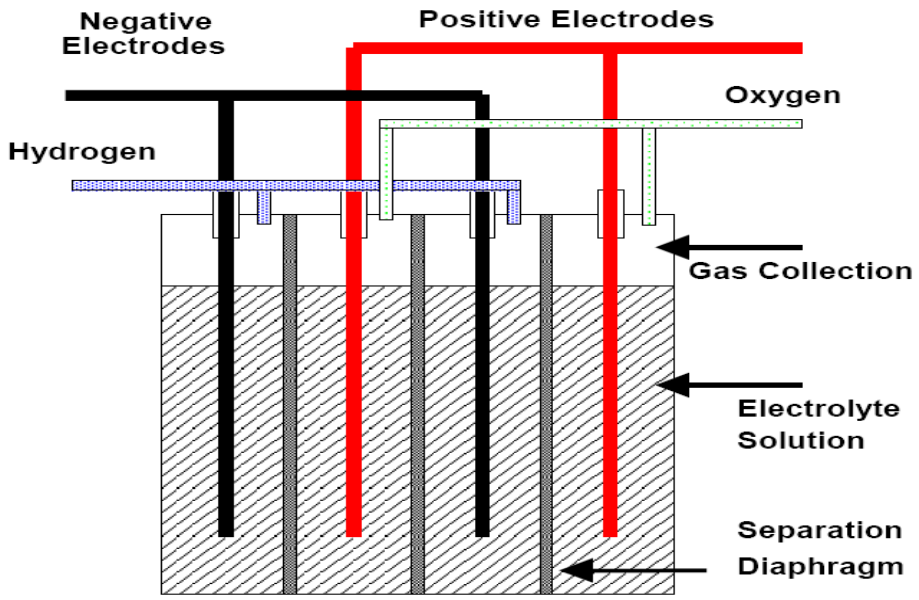


Figure 2.5: Unipolar Water Electrolyzer [22]

Alkaline electrolysis reactions are shown as follows,

Cathode (reduction): $2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$

Anode (oxidation): $4OH^-_{(aq)} \rightarrow O_{2(g)} + 2H_2O_{(l)} + 4e^-$

Net reaction: $2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)}$

In electrolyzers, because of the low conductivity of water, some chemical solutions must be added to increase the solution conductivity. Strong acid and strong alkali are applied as an electrolyte. Due to the severe corrosion of acid, instead of strong acid, the alkaline solutions are the primary electrolytes for water electrolysis. As an alternative to alkaline electrolysis, PEM (or polymer electrolyte membrane) electrolysis technology uses solid polymeric ion exchange materials in the electrolyzer. The advantages of solid polymer electrolyzers are shown as follows:

- Hydrogen gas can be generated at relatively high pressure in the solid polymer electrolyzer and the concentration of electrolyte is fixed
- There are no risk of pollution or spills caused by the aqueous electrolytes

- Low operating cost can be achieved with the high current density capacity of PEM electrolyzers

As illustrated in Figure 2.6, distilled water is first pumped to the deionizer and then is fed to electrolysis modules where water is split into hydrogen and oxygen gas. The mixture of hydrogen gas and water is sent to H_2/ H_2O separator. Hydrogen gas is extracted as a product while residual water is reused in the electrolyzer. Oxygen gas is generated at the anode and is extracted in the O_2/ H_2O separator. The heat of water electrolysis is recovered by the heat exchanger network. The energy consumed in the electrolyzers is supplied by direct electrical current (DC), which is transformed from the alternating current in the electrical converts.

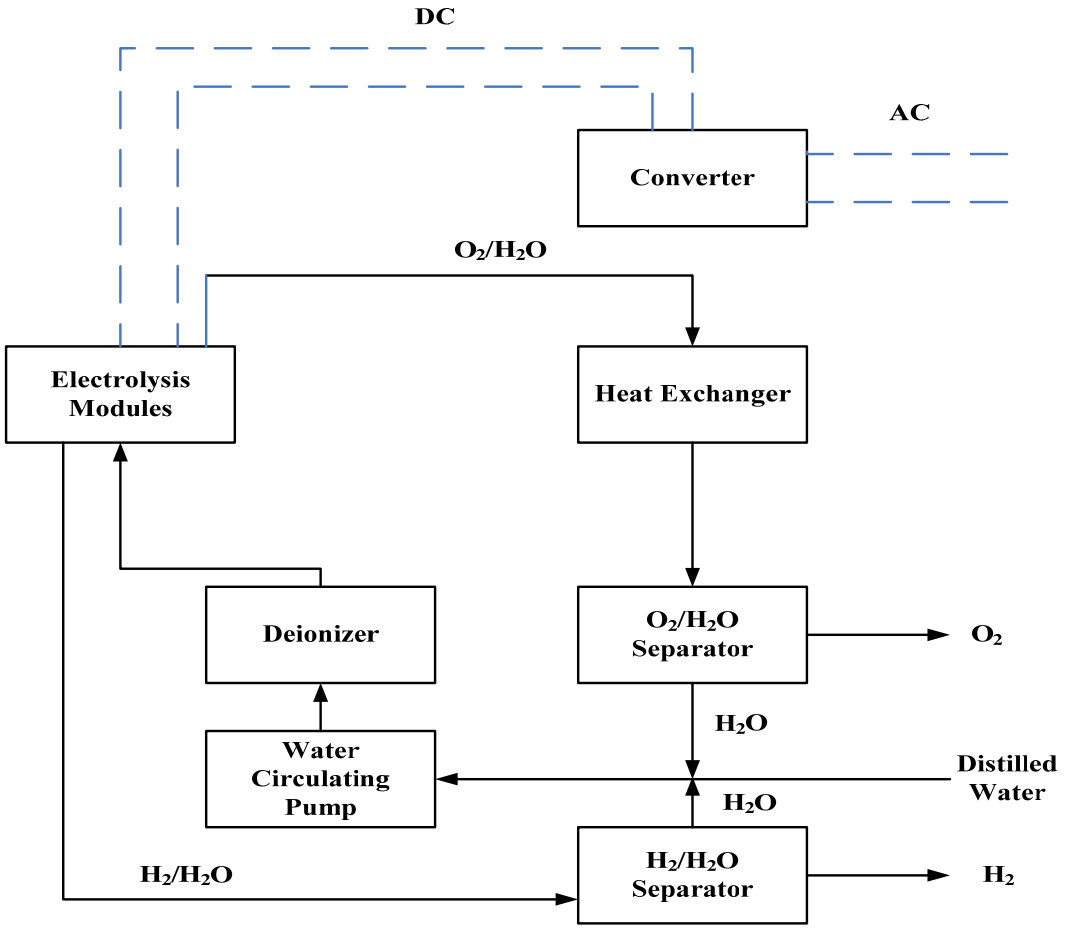


Figure 2.6: Conceptual Design of Water Electrolysis [18]

Alkaline and PEM electrolyzers are widely applied in industries. As shown in Table 2.2, a model from Norsk Hydro can produce over 1000 kg/day while the models from other manufacturers such as Teledyne Energy Systems Inc, Hydrogenics Corporation, and Proton Energy Systems Inc can generate less than 100 kg H_2/day. These hydrogen generation stations can be operated automatically with a control system and reliable safety measures. Due to modular design, these models can be easily paralleled to increase hydrogen production capacity. The components like electrolyzers, compressors, storage tanks and purification membrane are integrated into one compact system, thus higher conversion and energy efficiencies are achieved as displayed in Tables 2.3 and 2.4 [23].

Table 2.2 List of Hydrogen Generation Stations [23]

Manufacturer Model	Hydrogen Production Capacity kg/day
Proton HOGEN 20	1
Proton HOGEN 40	2
Proton HOGEN 380	22
HySTAT S	10-15
HySTAT D	30
HySTAT Q	60
Teledyne HM-200	24
Teledyne EC-500	60
Teledyne EC-750	91
Norsk Atmospheric Type No. 5020(4000Amp DC)	324
Norsk Atmospheric Type No. 5030(4000Amp DC)	647
Norsk Atmospheric Type No. 5040(4000Amp DC)	813
Norsk Atmospheric Type No. 5040(5150Amp DC)	1046

Conversion efficiency is defined as mass of products, hydrogen and oxygen, divided by mass of reactants, water. As demonstrated in Table 2.3, conversion efficiency of electrolyzers ranges from 80-95%. Energy efficiency is defined as higher heating value (HHV) of hydrogen divided by electrolyzer energy consumption. The efficiencies of electrolyzers as displayed in Table 2.4 show that about 64-73% of the total consumed energy is converted to hydrogen product in electrolyzers.

Table 2.3: Conversion Efficiency of Hydrogen Generation Stations [23]

Model	Reactants kg/hr	Product H2 kg/hr	Product O2 kg/hr	Conversion Efficiency %
Teledyne EC-750	42	3.8	30	80
Proton HOGEN 380	8.4	0.9	7.1	95

Table 2.4 Energy Efficiency of Hydrogen Generation Stations [23]

Model	System Consumed Energy kWh/kg	Higher Heating Value kWh/kg	System Efficiency %
Teledyne EC-750	62.3	39	63
Proton HOGEN 380	70.1	39	56
Norsk Atmospheric Type No. 5040(5150Amp DC)	53.5	39	73

2.5.5 High Temperature Steam Electrolysis

Similar to water electrolysis, High temperature steam electrolysis (HTSE) is an electrolytic process as well, but instead of water steam is fed to the electrolyzers at the temperature of 700-1000ºC [25]; electrolyzers of HTSE are also different from water electrolysis. The reactions at the anode and the cathode are shown as follows [26]:

Cathode reaction: $H_2O + 2e^- \rightarrow H_2 + O^{2-}$

Anode reaction: $O^{2-} \rightarrow 1/2O_2 + 2e^-$

Net reaction: $H_2O \rightarrow H_2 + 1/2O_2$

As illustrated in Figure 2.7, steam is supplied to the electrolyzer and dissociates into hydrogen gas and oxygen ions. Hydrogen gas is accumulated and generated at the cathode while oxygen ions pass through the dense electrolyte and receive electrons to generate oxygen gas at the anode.

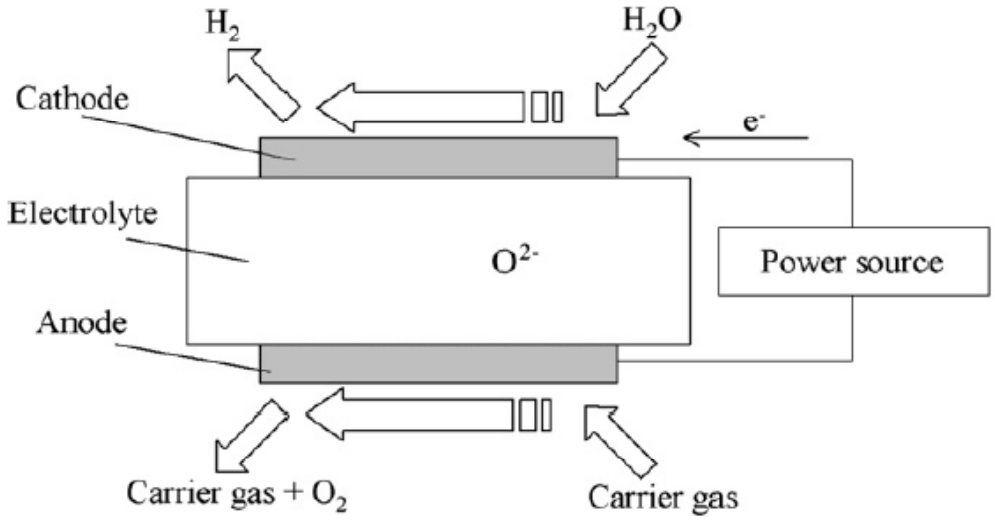


Figure 2.7: Principle of High Temperature Steam Electrolysis [24]

Compared with conventional water electrolysis, heat is introduced and less electricity is consumed in HTSE. The efficiency of HTSE from heat to hydrogen is projected to be up to 55% [27]; with regard to energy loss from electricity generation, theoretically the efficiency from heat

to hydrogen in HTSE is higher than water electrolysis due to less power consumption [28].

As shown in Figure 2.8, HTSE is generally coupled with a high temperature nuclear reactor as the operating temperature of HTSE is over 800ºC. The nuclear reactor supplies heat and electricity to the electrolyzers. A gas medium circulates through the nuclear reactor and the heat exchangers to provide the heat to the electrolyzers. This technology is still at early stage as suitable durable membranes need to be developed.

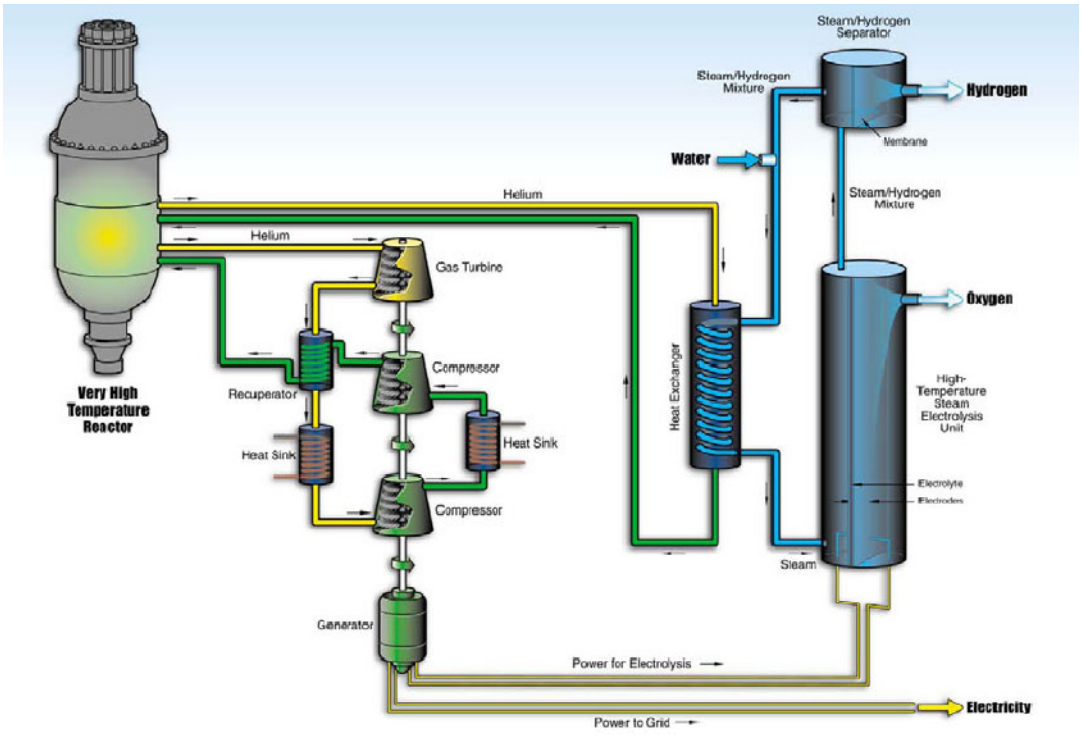


Figure 2.8: Conceptual Design of High Temperature Electrolysis plant [29]

2.5.6 Thermochemical Cycles

In thermochemical cycles, water is split into hydrogen and oxygen at the temperature of over 750ºC [30]. Since the 1960's, over 100 thermochemical cycles have been studied [31], but currently researchers mainly concentrate on three cycles, sulphur-iodine (S-I), Calcium-bromine-iron (UT-3) and copper-chlorine (Cu-Cl). The efficiencies of thermochemical processes were projected to be above 40%. The reactions of proposed thermochemical cycles are

shown as follows,

Ca-Br-Fe (UT-3) cycle [32]

$CaBr_2 + H_2O \rightarrow CaO + 2HBr$ (730ºC)

$CaO + Br_2 \rightarrow CaBr_2 + 1/2O_2$ (550ºC)

$Fe_3O_4 + 8HBr \rightarrow 3FeBr_2 + 4H_2O + Br_2$ (220ºC)

$3FeBr_2 + 4H_2O \rightarrow Fe_3O_4 + 6HBr + H_2$ (650ºC)

Cu-Cl Cycle [33]

Hydrolysis Reaction

$2CuCl_2 + H_2O \rightarrow Cu_2OCl_2 + 2HCl$ (400ºC)

Oxychloride Decomposition

$Cu_2OCl_2 \rightarrow 2CuCl + ½\ O_2$ (500ºC)

Electrolysis

$2CuCl + 2HCl \rightarrow 2CuCl_2 + H_2$ (70ºC)

S-I cycle [34]:

Bunsen Reaction:

$I_2+SO_2+2H_2O \rightarrow 2HI+H_2SO_4$ (20-120ºC)

Decomposition of Sulfuric acid:

$H_2SO_4 \rightarrow 1/2O_2+SO_2+H_2O$ (800-900ºC)

Decomposition of Hydrogen Iodide:

$2HI \rightarrow H_2+ I_2$ (350-500ºC)

All of these three cycles are at early stage for the potential applications. The S-I cycle is the most promising cycle and many research institutions have started their projects. In the United States,

General Atomics, Sandia National Labs (SNL) and University of Kentucky are working on the development and optimization of S-I process, are endeavouring to achieve a high efficient separation of HI from water and excessive iodine through reactive distillation, and explore the best distillation schemes. In Japan, Japan Atomic Energy Agency (JAERI) has implemented a 48-hour bench-scale test for the S-I cycle, in which 45 litres of hydrogen were generated. Another 50 litres of hydrogen test will be started and a test on a pilot plant is on the way [35-36]. In Europe French Atomic Energy Commission (CEA), Emprasarios Agrupados, University of Rome and University of Sheffield also started their projects in 2004 [37].

The studies of UT-3 cycle are currently focused on investigating cycling behaviours and extrapolating to an industrial scale from the conceptual design. The measures such as applying a fluidized bed reactor and simplifying the cycle by a two-twinned reactor design are implemented to improve process efficiency [35]. Compared with the other two cycles, the studies of Cu-Cl cycle are still at very early research stage. Argonne National Laboratory, International Nuclear Energy Research Initiative (INERI), Atomic Energy of Canada Ltd, and Nuclear Research Initiative Consortium (NERI-C) are investigating this cycle. An Aspen model and conceptual design were built to explore the feasibility of cycle process. The future work will be targeting a quantitative model for hydrolysis and electrolysis reaction, an effective membrane to avoid Cu crossover, and the system optimization [38].

The commercial potential for such cycles has yet to be demonstrated. These cycles all make use of hazardous chemicals at high temperatures in complex chemical processes. As such these processes are only suitable for large scale centralized production, and all these processes involve at least one high temperature cycle, which only the high temperature nuclear reactor can supply to the heat. The current status of thermochemical cycle research and the required nuclear technology advancements by the processes indicate that the full commercialization of the

processes is still decades away.

2.6 Hydrogen Storage

Hydrogen can be stored in a few ways like compressed gas storage, cryogenic liquid storage and metal hydride storage, but all storage methods require a great amount of energy and cost of storage is expensive.

2.6.1 Liquid hydrogen storage

Hydrogen liquefaction process consumes plenty of energy due to low normal boiling point of hydrogen, -235ºC [39]. The liquefaction process needs compressors, heat exchangers, a throttle valve or an expansion engine. As illustrated in Figure 2.9, hydrogen is first compressed and then pre-cooled by the liquid nitrogen, which is liquefied in another liquefaction cycle, and is cooled further through the heat exchangers. After the isenthalpic expansion through a throttle valve, hydrogen is liquefied and is extracted from the bottom of the separator. The remaining hydrogen gas is sent back to the cycle. An alternative to the pre-cool Linde process is the ideal liquefaction [39].

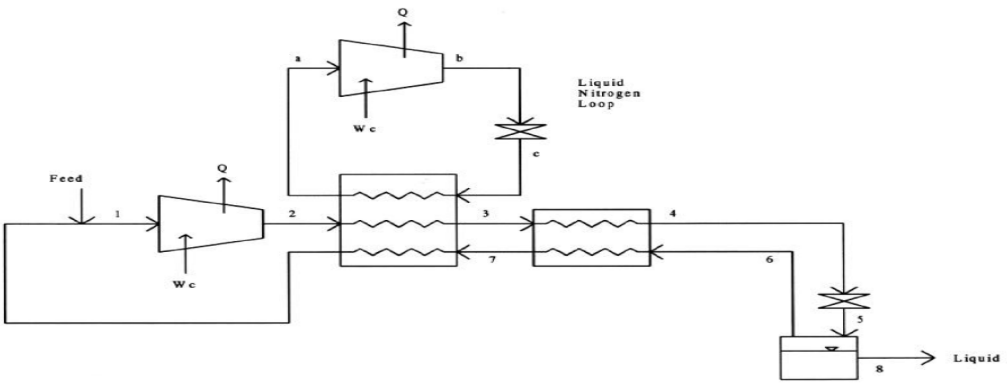


Figure 2.9: Flowsheet of Pre-cool Linde Liquefaction Process

As demonstrated in Figure 2.10, instead of the throttle valve, an expansion engine is applied to implement the reversible expansion process to cool hydrogen and liquefy hydrogen. The work of

hydrogen liquefaction is 3.228kWh/kg. Other similar processes are Dual-Pressure Linde Process, Claude Cycle, Dual-Pressure Claude, and Haylandt Cycle.

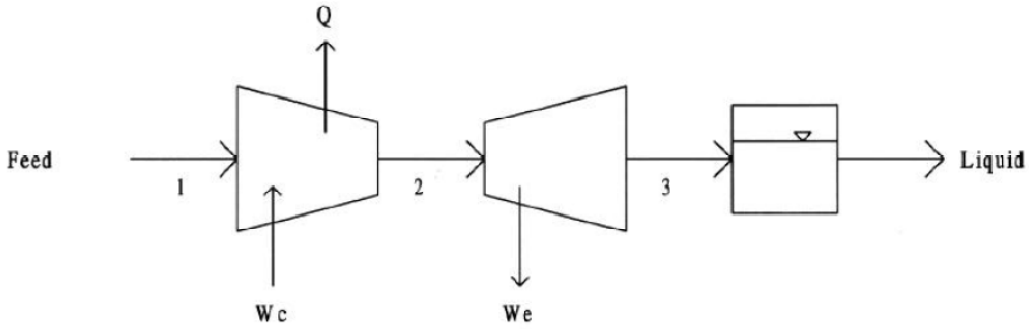


Figure 2.10: Flowsheet of Ideal Liquefaction Process

A liquid hydrogen container is generally designed as a double-wall vessel to minimize heat conduction, convection, and radiation. The space between walls is packed with layers of reflective and low emittance heat shielding material like perlite. An additional wall filled with liquid nitrogen can be also applied to minimize liquid hydrogen boil-off [39]. Liquid hydrogen storage is a potential for vehicular onboard storage. The volumetric capacity of liquid hydrogen is 0.07 kg/l, two times of hydrogen gas storage at 700 bars. With current insulation technology, heat transfer rates can be kept as low as about 1 W (in a 5 kg liquid hydrogen tank) to decrease the boil-off rate, but on the other hand high energy consumption of hydrogen liquefaction, about 40% of lower heating value (LHV) of hydrogen, is unavoidable[40]. The evaporation losses and storage safety are also concerned. For a vehicular onboard liquid hydrogen tank, after the inactivity period some amount of hydrogen has to be released to keep tank pressure at an acceptable level, but in a confined vehicular space the evaporated hydrogen may strand the vehicle and put the driver in danger.

Despite those limitations, liquid hydrogen storage is still a potential method for vehicular onboard storage with respect to higher storage density.

2.6.2 Metal hydride storage

Formation of metal hydride is a physical-chemical process. Hydrogen atoms diffuse from the outer surface of the metal inwards to the vacant metal atom crystal structure, and react with the metal atoms to form metal hydride. The formation of metal hydride reaction is exothermic while the decomposition reaction is endothermic.

As shown in Figure 2.11, hydrogen atoms start to diffuse and react with the metal atoms when the pressure increases and then the metal hydride reaction continues at the constant pressure until 90% of hydrogen storage is reached. The remaining 10% of hydrogen storage capacity can only be achieved when the pressure increases further. On the other hand, in order to release hydrogen from the metal hydride, the decomposition reaction can only be initiated at the higher pressure and higher temperature.

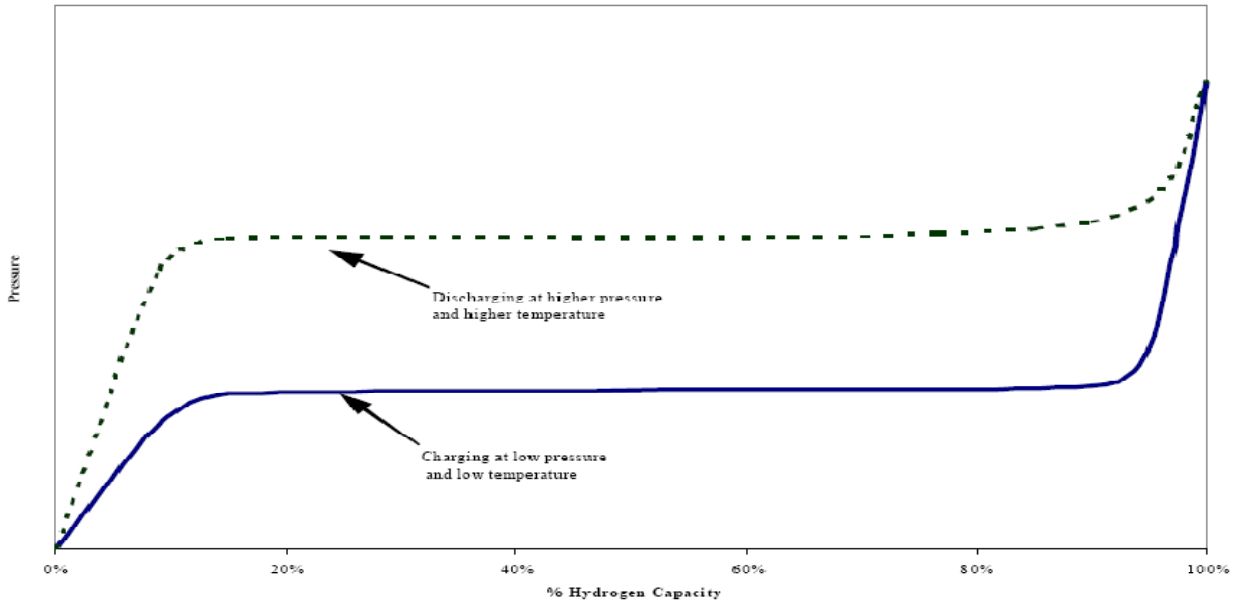


Figure 2.11: Metal Hydride Behaviour

The metal hydrides can contain about 4-12 % hydrogen by weight while the operating pressure is more than 10 MPa and the temperature of hydride decomposition is over 500°C. The current

research conducted by the Department of Energy (USA) is aiming to find lightweight metals and achieve higher volumetric and gravimetric density, and metal hydrides are certainly an option for vehicular onboard storage [41].

2.6.3 Compressed hydrogen gas storage

As shown in Figure 2.12, hydrogen can be stored in a pressure gas tank and compressed gas storage is the most common way to store gases, but because of low density of hydrogen gas, hydrogen storage pressure is generally higher than other gases and it results in higher operating cost and capital investment. The pressure of hydrogen gas storage ranges from 1.2-30 MPa in industries. Low-pressure storage tanks are applied widely in Europe and the capacities are generally about 115-400kg [39].

Figure 2.12: Hydrogen Gas Storage Tank

Compressed gaseous hydrogen is a potential for vehicular onboard storage. Compared with hydrogen liquefaction, hydrogen gas compression consumes less energy. Typically energy consumption of hydrogen gas compression is about 10% of lower Heating Value (LHV) of hydrogen, much less than hydrogen liquefaction, which requires about 40% of Lower Heating Value (LHV); compression energy for a hydrogen gas at 250-1000bar is about 2.5-4 kWh/kg, while conventional hydrogen liquefaction requires 10-14kWh/kg [40]. However the issues with

storage pressure, tank weight and cost are still the main difficulties for further application of gaseous hydrogen storage. In order to be stored in a vehicular compact tank, hydrogen gas must be compressed at a higher pressure, 350 or 700bar. A much higher pressure, 2000bar is being investigated to achieve higher volumetric density for greater vehicle driving distance, but the increase of storage pressure needs great material improvements. With high strength-to-weight ratio, carbon fibre is a qualified material to construct high pressure compressed gaseous hydrogen tanks. Some carbon fibre reinforced storage tanks have been built and tested by Quantum Technologies. As shown in Figure 2.13, a hydrogen gas tank consists of two shells and a polymeric liner; the outer shell is to protect the storage tank from outside strike and damage while the inner shell is a carbon fibre-epoxy resin composite to resist high pressure and contain compressed hydrogen gas; the liner made of high molecular weight polymers is to prevent hydrogen permeation. Cost of carbon fibre is expensive, accounting for about 40-70% of the total tank cost, so at the next step Quantum Technologies will aim to decrease the cost of carbon fibre to 6 $/kg in the future [42-43].

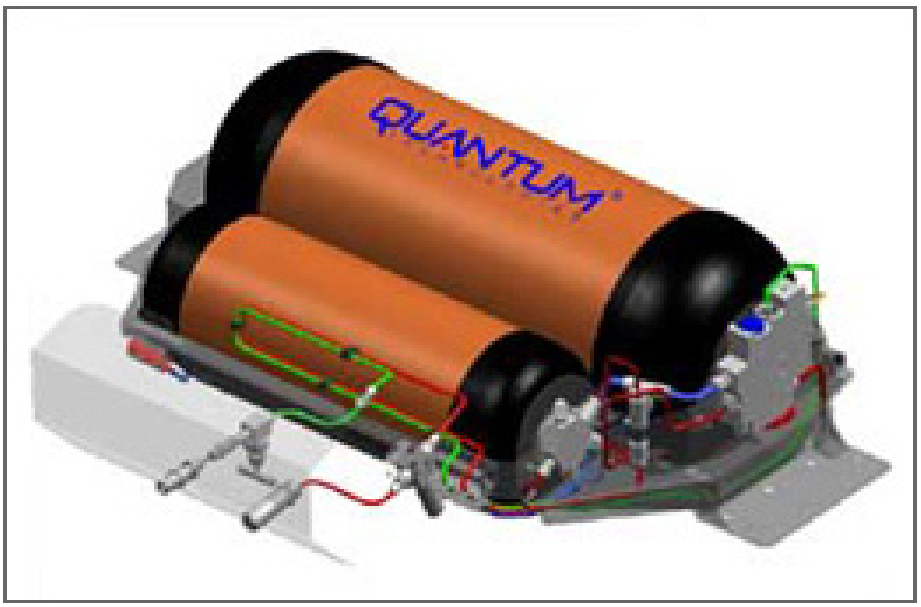


Figure 2.13: Carbon Fibre Reinforced Compressed Hydrogen Tank

2.7 Hydrogen Distribution

Hydrogen can be distributed as a liquid, a gas and a metal hydride. The following paragraphs will discuss these three distribution methods briefly.

Hydrogen gas can be distributed by high pressure cylinders, tube trailers, and pipelines. Pipeline distribution is economical for large scale production with respect to low density of hydrogen gas. Hydrogen gas pipelines were built in many countries like USA, Canada, and European Countries. The pipeline in Germany is 210 km long, and the longest one is from Air Liquide, 400km long from Northern France to Belgium. In northern Europe, the pipeline in the refineries and chemical complexes is totally about 1400km long. The United States has more than 720km hydrogen pipelines in total, and most of them locate along the Gulf Coast and Great Lakes [17, 39 and 44].

Liquid hydrogen is transported in a double-walled insulated tank to minimize boil-off. Some designers also apply liquid nitrogen heat shields to cool outer wall of the container. A cryogenic tank truck can carry 360-4300 kg of liquid hydrogen and the boil-off rate is about 0.3-0.4% / day.

Hydrogen can also be transported as a metal hydride, which is loaded on a truck or railcar and is discharged at the consumer site.

2.8 Studies of Hydrogen Pathways

As discussed in the previous sections, various energy resources, chemical processes, storage and distribution methods are available to produce and deliver hydrogen to consumers. Combinations of these options can generate different pathways to supply hydrogen, and thus the resulting cost of hydrogen also varies from each other. The ultimate goal of pathway studies is to achieve a cost-effective and eco-friendly route to generate and deliver hydrogen. The Department of Energy of USA has started a series of hydrogen pathway studies and the following will demonstrate conceptual designs of these pathways [3].

2.8.1 Distributed Steam Methane Reforming Hydrogen Production Pathway [3]

As shown in Figure 2.14, distributed steam methane reforming (SMR) technology is utilized to produce and supply hydrogen onsite. Since distributed facilities require low capital investment and SMR process is fully commercialized, cost of hydrogen from this pathway is lower than other options at current natural gas price. So this pathway may be suitable for the near term of hydrogen economy development. Note that this pathway is cost-effective but not eco-friendly due to large amount of carbon dioxide emissions from SMR process. However, at the early stage of hydrogen economy, low cost of product may give the market an easy commencement.

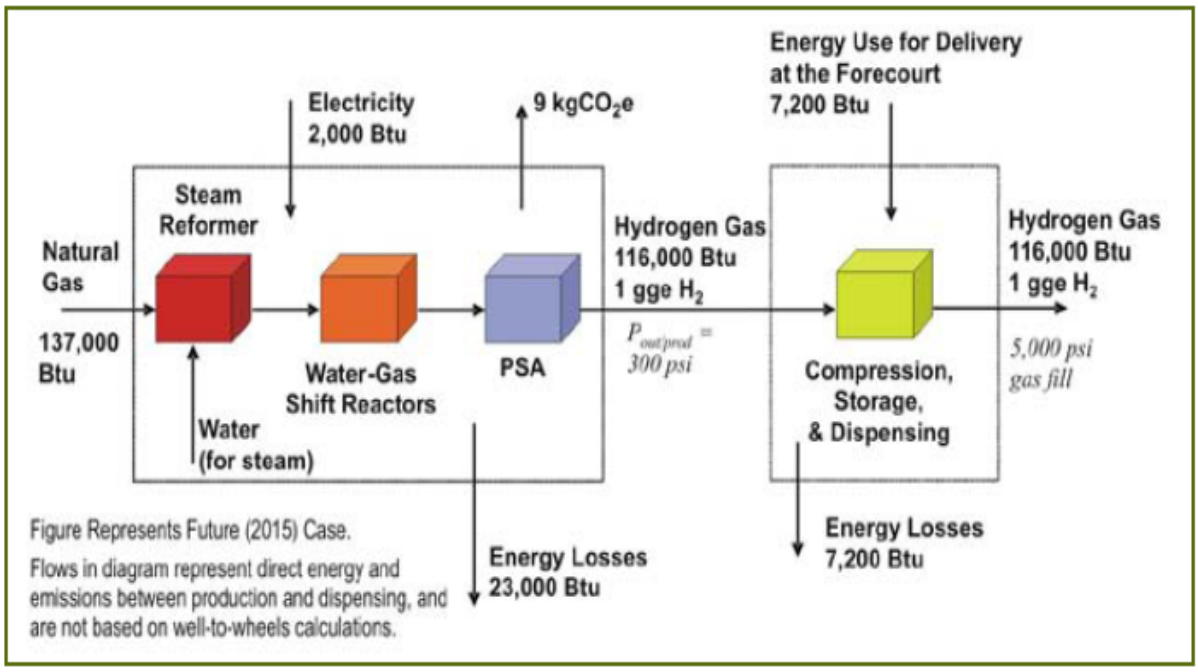


Figure 2.14: Distributed Steam Methane Reforming Pathway

As shown in table 2.5, the achieved efficiency of methane reforming process and the efficiency of the pathway from well to the refueling station are 69% and 66% respectively, and with the future SMR technology improvement the two efficiencies can reach 83% and 79% correspondingly in 2015, highest efficiencies among the studied pathways, but one should notice that this pathway is

not a zero emission route with respect to carbon dioxide emission from the process.

Table 2.5: Parameters and Results of Distributed SMR Pathway [3]

	Current (2005) Distributed SMR - FCV	Future (2015) Distributed SMR - FCV
Natural Gas Feedstock Price ($/million Btu LHV)	5.24	5.24
Natural Gas Feedstock Price ($/thousand scf)	5.15	5.15
Energy in Natural Gas Feedstock (Btu)	165,000	137,000
Electricity Price ($/kWh)	0.076	0.076
Electricity to Process (Btu)	2,000	2,000
Energy Losses from Process (Btu)	51,000	23,000
Pressure of Hydrogen from Production (psi)	300	300
Energy Use for Delivery at Forecourt (Btu)	7,200	7,200
Energy Use for Delivery Transport (Btu)	N/A–Forecourt Production	N/A–Forecourt Production
Hydrogen Dispensing Fill Pressure (psi)	5,000	5,000
Plant Gate Energy Use Including Feedstock (Btu)	167,000	139,000
Production Process Efficiency	69%	83%
Pathway Efficiency	66%	79%
Greenhouse Gas Emissions from Production (lb/gge of hydrogen produced)	24	20

Figure 2.15 demonstrates cost percentage of the pathway. The costs of capital investment and natural gas feedstock are the major parts, occupying 44% and 30% of total cost respectively; the study also showed that cost of hydrogen was estimated to be 3.10$/gge (gasoline gallon equivalent) in 2005, and was projected to be 2.00$/gge (gasoline gallon equivalent), but one should notice that the price of natural gas was fixed at 5.15$/thousand scf (standard cubic feet) from 2005 to 2015, which is not realistic with respect to recent increase of energy prices.

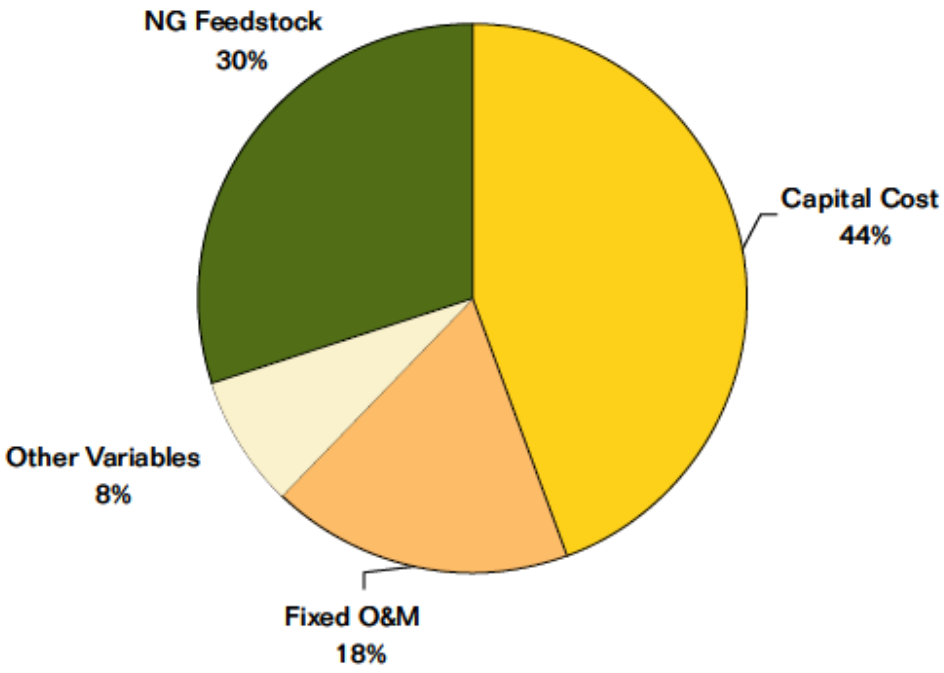


Figure 2.15: Cost Breakdown of Distributed Steam Methane Reforming Pathway

2.8.2 Distributed Wind Turbine Hydrogen Production Pathway [3]

As shown in Figure 2.16, wind energy is used to generate hydrogen to minimize greenhouse gas emissions from the process and grid electricity is a supplement in case wind energy is insufficient in some specific weather conditions. Note that capital cost of power generation for the grid electricity is not included in the analysis.

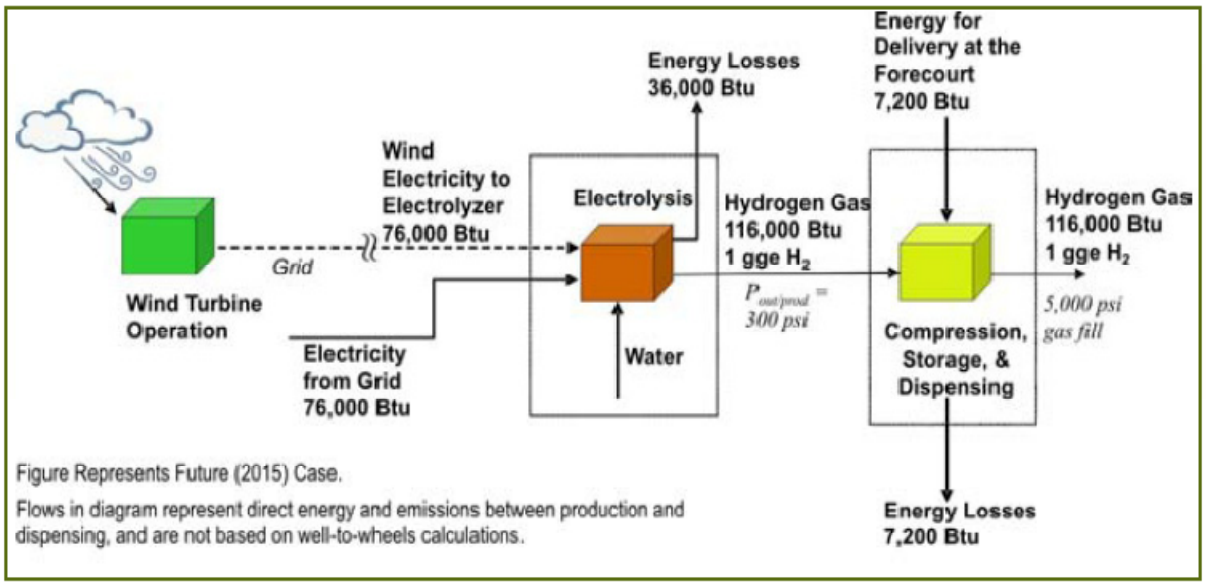


Figure 2.16: Distributed Wind Turbine Hydrogen Production Pathway

As displayed in Table 2.6, the process efficiency and the pathway efficiency are 64% and 61% respectively, lower than the steam methane reforming process; cost of hydrogen from this pathway is 5.70$/gge (gasoline gallon equivalent), higher than the steam methane reforming process, but this pathway has less greenhouse gas emission. So, this distributed wind turbine hydrogen production pathway can be a good option for the transition to a hydrogen economy, but the locations of production facilities are geographically restrained with respect to the dependence on wind condition.

Table 2.6: Parameters and Results of Wind Hydrogen Production Pathway [3]

	Current (2005) Distributed Electrolysis Using Wind/Grid - FCV	Future (2015) Distributed Electrolysis Using Wind Energy - FCV
Feedstock Price ($/million Btu)	N/A - Wind Energy	N/A - Wind Energy
Energy in Feedstock (Btu)	N/A - Wind Energy	N/A - Wind Energy
Grid Electricity Consumed (kWh)	40	24
Electricity Price ($/kWh)	0.052	0.038
Electricity to Process (Btu)	182,000	152,000
Energy Losses from Process (Btu)	66,000	36,000
Pressure of Hydrogen from Production (psi)	300	300
Energy Use for Delivery at the Forecourt (Btu)	7,200	7,200
Energy Use for Delivery Transport (Btu)	N/A - Forecourt Production	N/A - Forecourt Production
Hydrogen Dispensing Fill Pressure (psi)	5,000	5,000
Plant Gate Energy Use Including Feedstock (Btu)	182,000	152,000
Production Process Efficiency	64%	76%
Pathway Efficiency	61%	73%

2.8.3 Centralized Biomass Gasification Hydrogen Production Pathway [3]

Centralized hydrogen production will be required to meet the demands from FCVs when hydrogen fuel cell vehicle market expands. Since production facilities are utilized at one site, cost of hydrogen can decrease to some extent, but on the other hand greater amount of capital investments will be needed for the installation of large scale production, storage and delivery facilities. As shown in Figure 2.17, centralized biomass gasification technology is applied to generate hydrogen on this pathway.

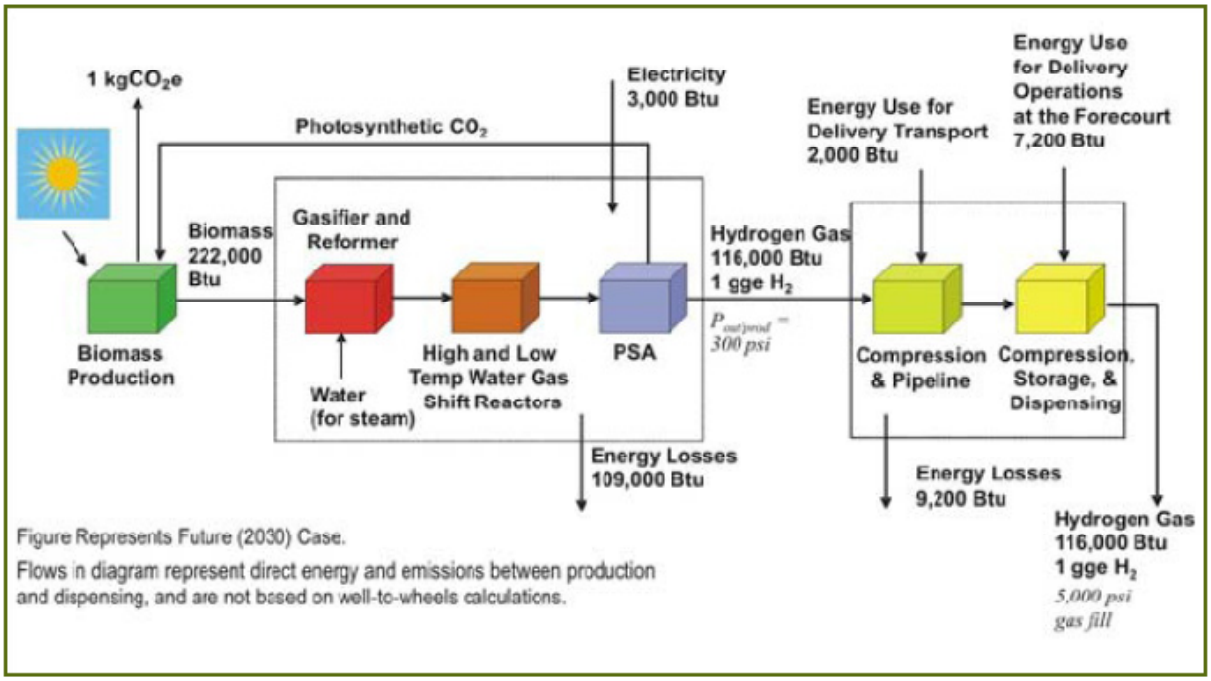


Figure 2.17: Biomass Gasification Hydrogen Production Pathway

The parameters and results are displayed in Table 2.7. The process efficiency and the pathway efficiency are 45% and 40% respectively, and the cost of hydrogen was projected to be 5.10$/gge (gasoline gallon equivalent). Considering the greenhouse gas emissions from the gasification process, biomass gasification pathway can be a supplement instead of a primary option. The main limitations for this pathway will be availability of feedstock, and /or the transportation of the feedstock to a centralized location. Also, there will be competition for the feedstock for the production of other bio-fuels such as ethanol and bio-diesel. Purification of this gas to a suitable hydrogen gas feedstock will take significant effort and energy, and use of this feedstock directly in a low speed diesel engine is likely more practical.

Table 2.7: Parameters and Results of Biomass Gasification Hydrogen Production Pathway [3]

	Current (2005) Biomass Gasification - FCV	Future (2030) Biomass Gasification - FCV
Biomass Feedstock Price ($/million Btu LHV)	2.26	2.26
Biomass Feedstock Price ($/bone dry ton)	38.00	38.00
Energy in Biomass Feedstock (Btu)	252,000	222,000
Electricity Price ($/kWh)	0.052	0.052
Electricity to Process (Btu)	5,000	3,000
Energy Losses from Process (Btu)	141,000	109,000
Pressure of Hydrogen from Production (psi)	300	300
Energy Use for Delivery Operations at the Forecourt (Btu)	Negligible	7,200
Energy Use for Delivery Transport (Btu)	34,000	2,000
Hydrogen Dispensing Fill Pressure (psi)	5,000	5,000
Plant Gate Energy Use Including Biomass (Btu)	257,000	225,000
Production Process Efficiency	45%	52%
Pathway Efficiency	40%	49%
Greenhouse Gas Emissions from Production (lb/gge of hydrogen produced)	2.3	2.0

2.8.4 Centralized Nuclear Sulfur-Iodine Hydrogen Production Pathway [3]

As displayed in Figure 2.18, a dedicated nuclear reactor supplies the sulfur-iodine reactor high temperature heat to generate the hydrogen products. Since this pathway is to convert the heat directly into the hydrogen energy and unlike other options there is no conversion of heat to electricity and electricity to hydrogen energy, it has the potential to be most efficient way to generate hydrogen. As a chemical process, thermochemical cycles are also more suitable for the large scale centralized production than electrolytic processes. However since the thermochemical technologies are still at early phase of research, currently they can't be fully applicable and the efficiencies of thermochemical cycles are not as good as expected.

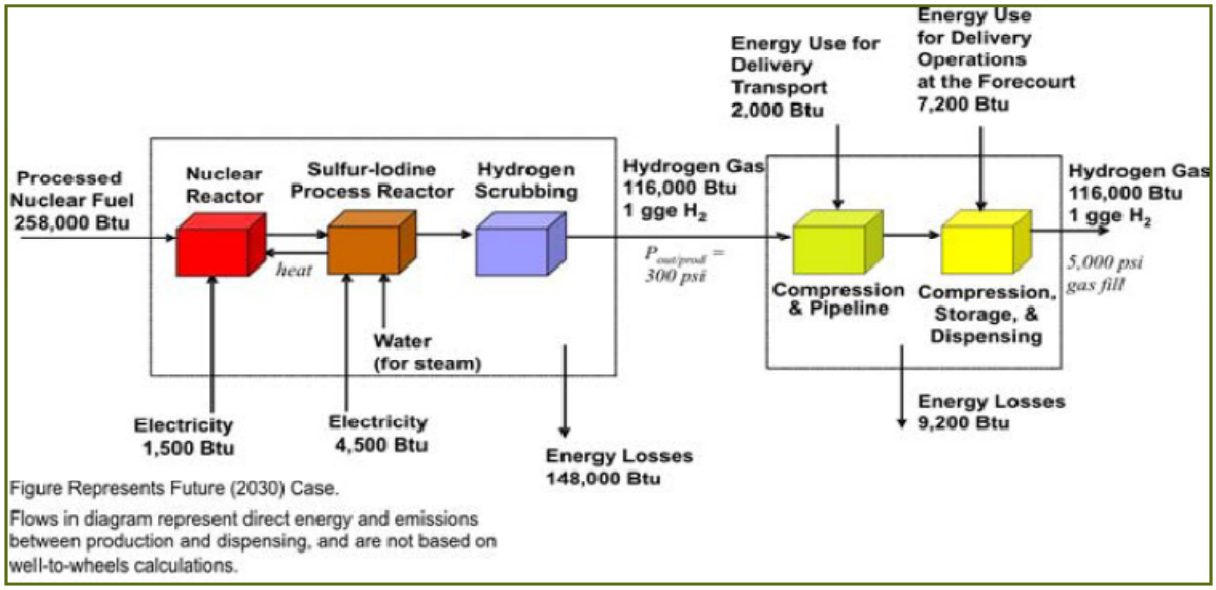


Figure 2.18: Nuclear Sulfur-Iodine Hydrogen Production Pathway

Cost of hydrogen from this pathway was projected to be 3.20$/gge (gasoline gallon equivalent) in 2030. As displayed in Table 2.8, the process efficiency and pathway efficiency were projected to be 44% and 42% respectively in 2030, which are the lowest efficiencies among options due to the immaturity of the technology. At the current stage, thermochemical hydrogen production technologies still need the breakthrough advancements.

Table 2.8: Parameters and Results of Nuclear Sulfur-Iodine Pathway [3]

	Future (2030) Nuclear Sulfur Iodine - FCV
Nuclear Cycle Feedstock Price	See note #8
Energy in Feedstock (Btu)	258,000
Electricity Price ($/kWh)	0.052
Energy Losses from Process (Btu)	148,000
Pressure of Hydrogen from Production (psi)	300
Energy Use for Delivery at the Forecourt (Btu)	7,200
Energy Use for Delivery Transport (Btu)	2,000
Pressure of Hydrogen from Dispenser (psi)	5,000
Plant Gate Energy Use Including Feedstock (Btu)	264,000
Production Process Efficiency	44%
Pathway Efficiency	42%

2.9 End-uses of Hydrogen and Fuel Cell Technologies

Hydrogen is widely used in industries. Approximate 16 trillion cubic feet of hydrogen are consumed in the world each year [44]. Hydrogen is mainly applied in two areas, manufacturing ammonia and refining crude oil. Ammonia is an important intermediate of fertilizers, and hydrogen is a reactant of ammonia synthesis reaction. In refining industries, hydrogen is applied in the process of hydrocracking and hydrogenation to produce gasoline, heating oil and other petroleum products. Hydrogen is also involved in the manufacturing of some commercial products such as dyes, drugs, plastics, vitamins, cosmetics, and cleaners. In power generation plants, hydrogen is also used as a sealing and cooling gas in the rotating equipments. Liquid hydrogen is applied in space industries as the main fuel of rockets. Generally, hydrogen is mostly used as a chemical intermediate material, and is produced and consumed onsite. In the recent years, the hydrogen applications on fuel cells are attracting more attention. As fuel cell technologies become more mature, hydrogen will become a “green” energy replacement of fossil fuels in the transportation sector and hydrogen on board fuel cell technology can be applied to reduce the emission of “green house gases” (GHG) and other gas pollutants from automobiles significantly.

The first workable fuel cell was built by William Grove in 1839. In this fuel cell, hydrogen and oxygen were consumed while the platinum plates worked as the electrodes and sulfuric acid was used as the electrolyte. In the 1960s, the onboard fuel cells were developed to supply the power to the Gemini and Apollo spacecraft by NASA. In the 1990’s, some major progresses were achieved to make fuel cell technologies more commercialized, and now fuel cells can be applied in stationary power generation plants, mobile power generation devices, cars and other transportation facilities.

2.9.1 Working Principle of Fuel Cells

The key technology for hydrogen economy is hydrogen fuel cell. Hydrogen fuel cell allows for direct high efficient conversion of hydrogen to electricity. Process of fuel cells is to convert chemical energy of a fuel and an oxidant to electrical energy. As illustrated in Figure 2.19, a fuel cell consists of an anode, a cathode and an electrolyte layer. In a hydrogen fuel cell, hydrogen is fed as a fuel to the anode while oxygen works as an oxidant on the cathode. Hydrogen atoms are split into protons and electrons with the help of a catalyst on the anode. Protons pass through porous structural electrolyte to the cathode while electrons are utilized in the external electrical circuit and eventually water is formed.

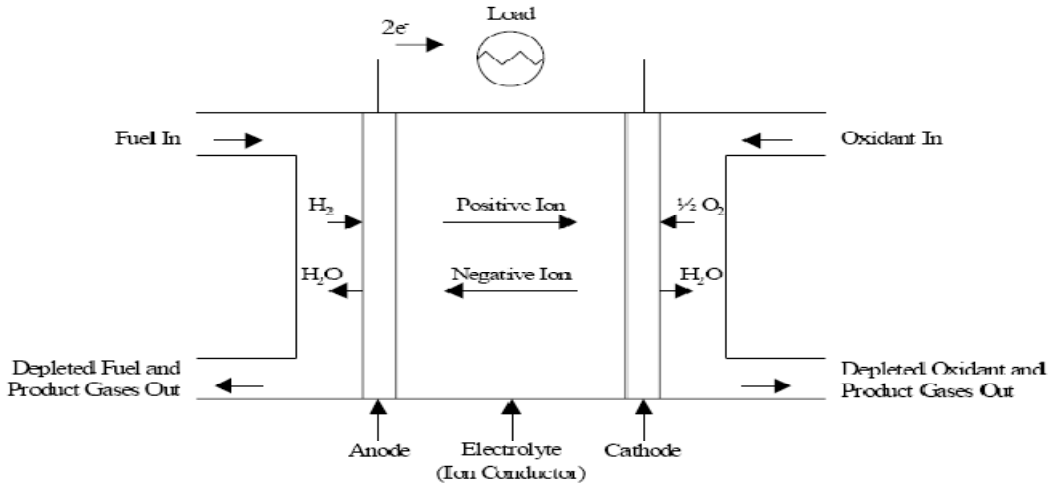


Figure 2.19: Schematic of Fuel Cell [45]

2.9.2 Types of Fuel Cells

After decades of technology evolution, various types of fuel cells have been developed. With the respect to different electrolytes and cell configurations, fuel cells are generally categorized into five classes, Polymer Electrolyte Membrane (PEM), Solid Oxide (SOFC), Alkaline (AFC), Phosphoric Acid (PAFC), and Molten Carbonate (MCFC) [46].

- Polymer Electrolyte Membrane: a solid polymer membrane is applied as an electrolyte. On

the electrodes noble metal catalysts can facilitate the process, but on the other hand noble metal catalysts also account for the major cost of fuel cells. Since the materials of membrane are sensitive to high temperature and the catalysts can be poisoned by impurities in hydrogen gas, polymer electrolyte membrane fuel cells can only operate at about 80-100°C and highly purified hydrogen gas is a must for fuel cells' operation. PAFC are similar technology but with hot phosphoric acid as an electrolyte, and because of electrolyte corrosion issues PAFCs have been replaced by PEM.

- Solid Oxide: the electrolyte in solid oxide fuel cells is a hard non-porous ceramic compound and high temperature is required for the operation of fuel cells to achieve acceptable ionic conductivity. At the temperature of about 500-1000°C, the reaction can achieve approximately 45%-65% conversion efficiency and no expensive catalyst is required. However because of low conductivity of ceramic materials and slow system start-up, the applications of solid oxide fuel cells are restrained.
- Alkaline: the electrolyte in alkaline fuel cells is potassium hydroxide (KOH). The fuel cells can operate at 100-250°C, and no precious metal catalysts are required for the operation. Alkaline fuel cells are applied widely, but since the electrolyte is a basic solution, the operation of fuel cells is also sensitive to the CO_2 and CO impurities in the feed gases and high purity of hydrogen fuel is requested.
- Molten Carbonate: a molten carbonate mixture in a porous chemical ceramic lithium-aluminum oxide matrix is the electrolyte of fuel cells. The operating temperature is about 650°C and the efficiency can be up to 60%. In addition the fuel cell operation is insensitive to CO and C_{O2} impurities, which makes operation with hydrocarbons more suitable.

2.9.3 Fuel Cell Applications

Fuel cells are applied to generate electricity and the efficiency from fuel to electricity can approach 64% for PEM fuel cells. Due to low noise and gas pollutant emission, fuel cells can be used in stationary power co-generation plants to supply both heat and power to residential buildings, hospitals, hotels, offices, and schools. Stationary fuel cells can work as a backup power device to provide a reliable grid-independent energy. Small size of fuel cells can be used as a portable device to power cellular phones, laptops, and other electronic appliances. A major application of PEM/SOFC is in the transportation sector. On-board fuel cells can be installed in cars, buses, trains, and planes. Considering zero "green house" gas emission and air pollutant from hydrogen on-board fuel cells, the major automobile manufacturers like GM, Toyota, and Honda have already started their fuel cell vehicles projects, and hydrogen fuel cell vehicles are moving towards commercialization.

2.10 Hydrogen Purity and Security

High purity of hydrogen is required for PEM fuel cells and thus must be considered in the hydrogen production system. The impurities in hydrogen gas such as carbon dioxide, carbon monoxide, sulfur and ammonia can affect fuel cell durability and compromise performance of fuel cells. The allowable limits of impurities in hydrogen fuel are still under investigation, but as shown in Table 2.9, some existing standards and codes can be applied for current hydrogen applications. For more detailed information, one should consult specifically with the corresponding industrial standards and codes.

The properties of hydrogen and other common fuel gases are shown in Table 2.10. Since hydrogen is the lightest element, it can dissipate rapidly into the air. If the facilities are built in a confined area, once there is a hydrogen leak, hydrogen can accumulate very quickly and the concentration will reach the limit of flammability and detonatability very soon. Hydrogen can

be easily ignited and denoted and as the flame of hydrogen fire is invisible, thus it is hard to be sensed and very harmful to the people. Currently, hydrogen is generally applied in the industrial or laboratory areas and is handled by the certified technical personnel, but in the future with the widespread applications of hydrogen fuel cells ordinary people will have close contact with hydrogen, thus more comprehensive safety standards and codes must be established for the public safety. Table 2.11 lists some of standards and codes, but for the more detailed information, one should consult with the detailed industrial standards and codes.

Table 2.9: Hydrogen Purity Codes and Standards [47]

Organization	Codes, Standards, Regulations	Description
Defence Logistics Agency	MIL-PRF-27201C	Hydrogen, Gaseous, Type I, Propellant, Specification
Canadian Gas Association	CGA G-5.3	Specification requirements for commercially available gaseous and liquid hydrogen. Data on quality verification, sampling, analytical procedures, type uses for various grades and containers.
SAE	SAE J2719	Information Report on the Development of a Hydrogen Quality Guideline for Fuel Cell Vehicles
CGA	CGA P-6 Ed. 6	Standard Density Data, Atmospheric Gases and Hydrogen
International Organization for Standardization	ISO 14687-1999	Hydrogen Fuel-Product Specification

Table 2.10: Properties of Hydrogen and other Fuels [48]

Property	Hydrogen	Methane	Gasoline
Normal boiling point (°C)	-253	-162	37-205
Physical state at 25 °C, 1 atm.	Gas	Gas	Liquid
Heating value LHV(kJ/g) HHV(kJ/g)	 120 142	 50 55.5	 44.5 48
Flammability limits (vol. % in air)	4.0-75	5.3-15	1.0-7.6
Molecular weight (g/mol)	2.02	16.0	~107
Flame temperature in air (°C)	2045	1875	2200
Minimum ignition energy (MJ)	0.02	0.29	0.24
Quenching distance (mm)	0.64	2.0	2.0
Density at NBP (g/L)	70.8	423	~700
Vapour specific gravity at 25°C, 1 atm.	0.07	0.54	3.7

Table 2.11: Hydrogen and Fuel Cell Vehicles Safety Codes and Standards

Organization	Codes, Standards, Regulations	Description
National Fire Protection Association	BSR/NFPA2-200x	Hydrogen Technologies Codes
National Fire Protection Association	NFPA 30A-2008	Codes for Motor Fuel Dispensing Facilities and Repair Garages, 2008
National Fire Protection Association	NFPA 55-2003	Standard for the storage, use and handling of compressed gases and cryogenic fluid in portable and stationary containers, cylinders and tanks
Society of Automotive Engineers	SAE J2719	Information Report on the development of a hydrogen quality guidelines for fuel cell vehicles
Canadian Gas Association	CGA-5.4	Standard for hydrogen piping systems at consumer locations
Canadian Gas Association	CGA-5.5	Hydrogen Vent Systems
Canadian Gas Association	CGA-5.8	High pressure hydrogen piping system at consumer locations
International Code Council	ICC IFC-2006	International Fire Code, 2006
Society of Automotive Engineers	SAE J1766	Recommended practice for electric and hybrid electric vehicle battery systems crash integrity testing
Society of Automotive Engineers	SAE J 2572	Recommended Practice for measuring fuel consumption and range of fuel cell and hybrid fuel cell vehicles fuelled by compressed gaseous hydrogen
Society of Automotive Engineers	SAE J 2578	Recommended practice for general fuel cell vehicle safety

Chapter 3

Analysis of Ontario's Hydrogen Economy Demand from Hydrogen Fuel Cell Vehicles

3.1 Introduction

There is an increasing need for alternative fuels to meet the increasing the global energy demand, improve current urban air quality impacts and follow the treaty of global climate change [49]. According to Statistics Canada, energy demand in Canada has increased from 7384.7 petajoules in 2003 to 7643.2 petajoules in 2006 [50]. The global energy demand was projected to increase by over 60% by 2030 [51]. And globally about 18% of total energy consumption as well as 20% of the projected energy demand increment came from transportation sectors [52]. Automobile fuel combustion emits enormous amount of air pollutants. According to Environmental Protection Agency of US, in 2007, approximate 75% of carbon monoxide emission was contributed by highway vehicles and non-road mobile sources; nearly 50% of VOC emission came from highway vehicles. These air pollutants deteriorated urban air quality and affect human health. Scientific studies showed that air pollutants could cause some health problems such as aggravation of respirator, cardiovascular diseases, and cancers [53], and in Ontario over 1700 deaths a year were thought to be a result of poor urban air quality [54].Greenhouse Gas emissions from automobiles are also contributed to the global warming [55]. Hydrogen as a clean energy carrier can be a replacement of fossil oil in transportation sectors. An analysis showed that hydrogen could also be used as an energy storage medium that facilitated the implementation of intermittent renewable power sources such as wind and solar [4]. The emerging technology of onboard hydrogen fuel cells are near commercialization, and with the use of fuel cell powertrain, 1 kilogram hydrogen releases about the same energy as 1 gallon gasoline, not producing any

pollutant. Additionally, the overall energy efficiency of fuel cell vehicles is about two times of internal combustion vehicles (ICE) vehicles [56]. The main automakers have already developed a few fuel cell models, such as Hydrogen3 in 2002 from GM, Focus FCV from Ford, FCHV-5 in 2001 from Toyota, and FCX model in 1999 from Honda [57]. In recent years, GM and Honda have made some progress on fuel cell vehicle technology. GM presented its latest fuel cell vehicle model, Equinox Fuel Cell, and announced over 100 fuel cell vehicles in on-road trials. In 2008, Honda officially announced a lease program for the newest fuel cell model, FCX Clarity, and planed to lease 200 fuel cell vehicles in the first three years. In Canada, BC Transit is implementing a program to operate a 20-hydrogen hybrid fuel cell bus fleet in Whistler for the 2010 Olympic Winter Games [58]. Fuel cell vehicles are moving towards commercialization. In this chapter, three scenarios were built to describe and explore the trend of fuel cell vehicle market development, and a model was built to estimate hydrogen demand from all fuel cell vehicles in Ontario and the resulting costs of hydrogen production, storage, and distribution. Detailed flowcharts of the model were displayed in Appendix A.

3.2 Hydrogen demand from H_2 FCVS in Ontario

3.2.1 Flow Chart of Hydrogen Estimation Demand Model

In order to calculate the hydrogen demand first a model for the demand from one vehicle was constructed and a parallel model for the number of fuel cell vehicles in Ontario was developed as well. Figure 3.1 demonstrates flow chart of hydrogen estimation model logic applied in this work.

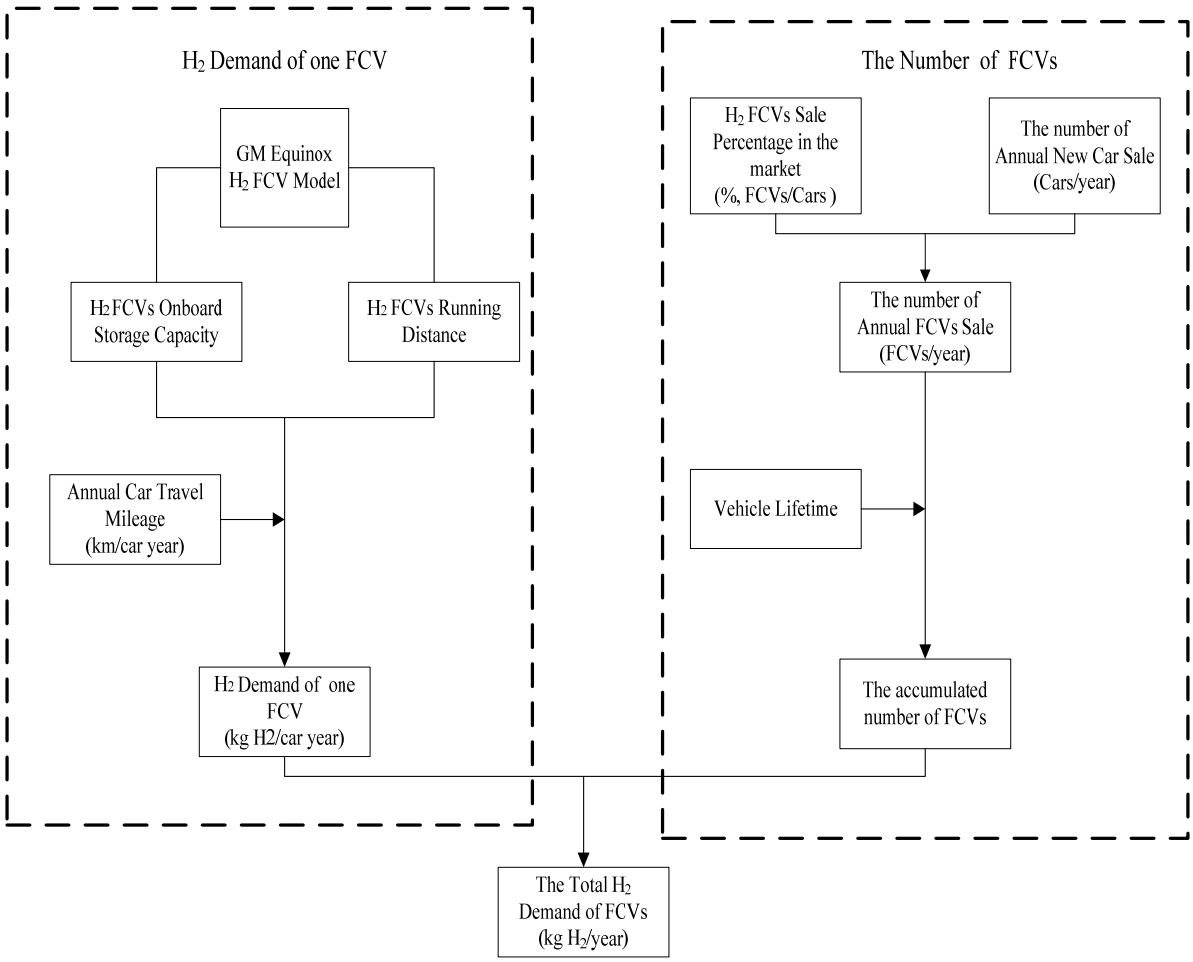


Figure 3.1: Flowchart of Hydrogen Demand Estimation Model

3.2.2 The number of FCVs in the future Ontario's Market

3.2.2.1 Scenarios of Hydrogen Powered Fuel Cell Vehicles Market Development

In order to calculate hydrogen demand in Ontario it is necessary to assume the uptake of FCVs. In this work it was assumed that the growth of hydrogen FCVs in Ontario would follow the similar trends as proposed for the U.S. market by Oakridge National Lab, and the scenarios from the report, "Integrated Analysis of Market Transformation Scenarios with HyTrans" [59]. The basic assumptions used were documented in Table 3.1, and three scenarios were built to describe the trend of the FCVs market development from 2015 to 2050. In this model number of vehicles in Ontario was assumed based on the current number and population growth. A market share for FCVs as a fraction of all new car sales for each year was assumed as follows.

Table 3.1: H_2 FCVs Market Development Assumption

Year	2015	2025	2050
Market Share(Scenario 1)	0	0.04	0.91
Market Share(Scenario 2)	0	0.05	0.95
Market Share (Scenario 3)	0	0.15	0.95

The year of 2015 was considered as H_2 FCVs start entering automobile market, and the year of 2025 was the time of H_2 FCVs starting growing rapidly, while the year of 2050 was assumed to be the time of H_2 FCVs taking control of new car market and essentially all new fuel cell vehicles were assumed to be hydrogen fuel cell vehicles. Scenario 1, 2 and 3 represented conservative, moderate and optimistic hydrogen fuel cell vehicle market development respectively. Based on H_2 FCVs market development assumptions above, logistic models will be established to estimate H_2 demand to service these vehicles.

3.2.2.2 Logistic Model

A study showed that logistic model could be applied to describe H_2 FCVs market development [60]. Logistic model was defined as follows,

$$P_{FCV} = \frac{1}{1 + \exp\left[-\left(a_{FCV} + b_{FCV}\left(t - t_0\right)\right)\right]} \quad (3.1)$$

Where, P_{FCV} is new H_2 FCVs market share (%)

a_{FCV} and b_{FCV} are coefficients of logistic models

t_0 is the year of H_2 FCVs entering new vehicle market, which is assumed to be 2015 for Ontario

t is time (year)

Note that in this chapter, new vehicles mean new light duty vehicles. It was assumed that light duty vehicles would be first and primary FCV market displacing the current widespread use of gasoline vehicles. Use logistic model and H_2 FCVs market share assumption in the previous part, and solve for a_{FCV} and b_{FCV} of each scenario. The achieved values of a_{FCV} and b_{FCV} are shown in Table 3.2

Table 3.2: Logistic model coefficients

Coefficient	a_{FCV}	b_{FCV}	$R^{\wedge 2}$
Scenario 1	-5.4025	0.2205	0.9999609
Scenario 2	-5.3225	0.2363	0.9999578
Scenario 3	-3.7206	0.1936	0.9988047

Input coefficients into the logistic model and H_2 FCVs market shares were achieved shown in Fig.3. 2.

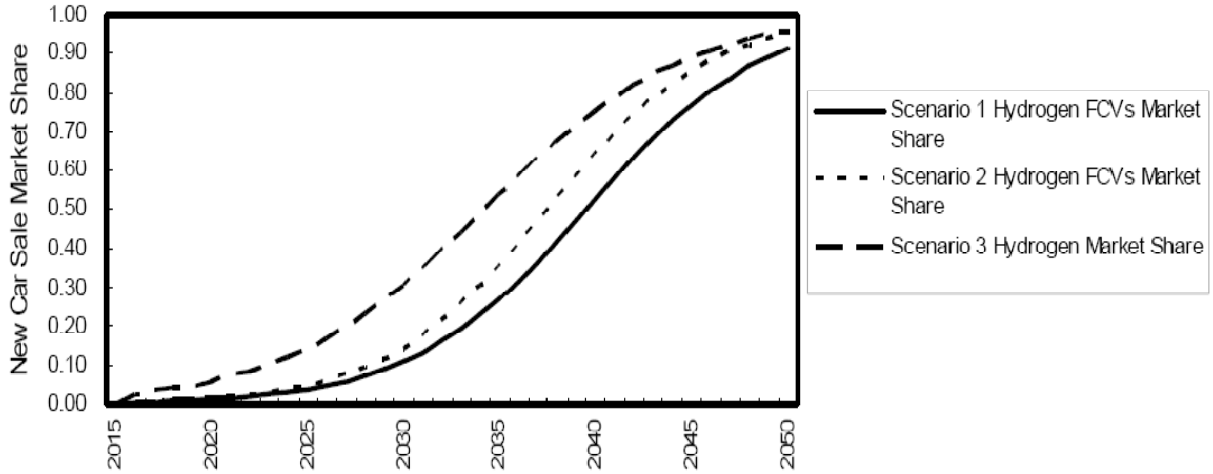


Figure 3.2: H_2 FCVs Market Sale

3.2.2.3 The number of New H_2 FCVs Sale in Ontario

Upon market share results achieved as shown in the previous section, the number of H_2 FCVs sold each year in Ontario was estimated as follows,

$$N_{FCV}=P_{FCV}\times N_{new\ car\ sale} \quad (3.2)$$

Where, N_{FCV} is the number of new H_2 FCVs sold each year in Ontario (vehicle)

$N_{new\ car\ sale}$ is the number of new vehicles sold each year in Ontario (vehicle)

In order to solve for N_{FCV}, the value of $N_{new\ car\ sale}$ needs to be achieved. Figure 3.3 shows the historical data of the number of new vehicle sale in Ontario from 1968-2007 [61].Through a linear regression on historical data, a pattern for the number of new vehicle sold in Ontario each year was estimated as shown below,

$$N_{new\ car\ sale}= -1.211\times10^{7}+6353t \quad (3.3)$$

Where, t is the time (year)

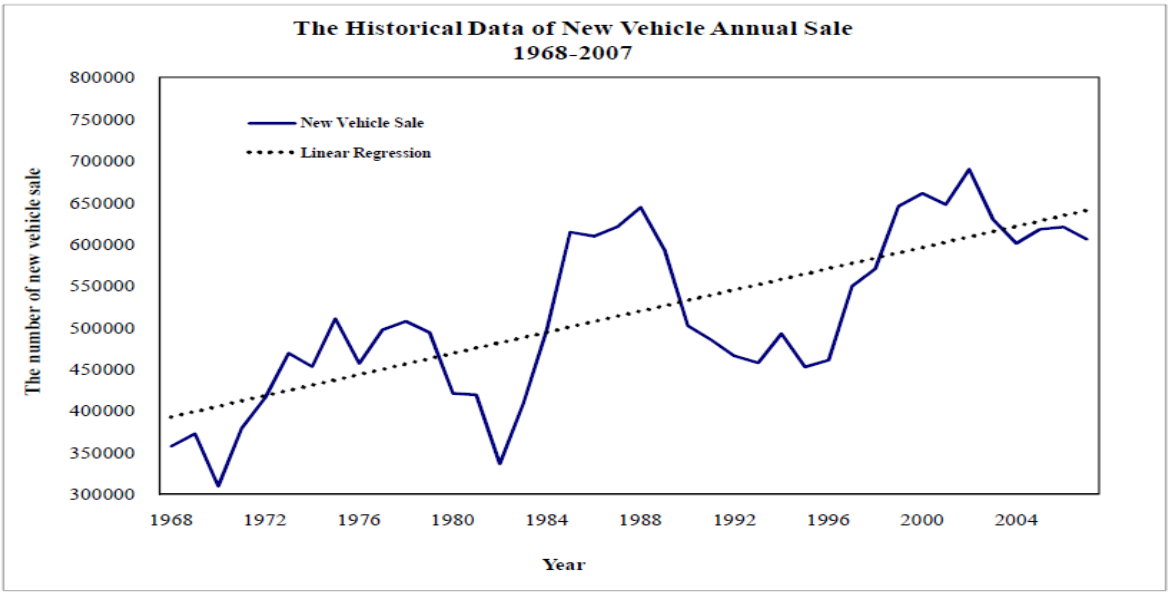


Figure 3.3: Historical Data of Ontario's New Vehicle Sale

As shown in Figure 3.4, hydrogen fuel cell vehicles enter the market in 2015, start market penetration in 2015, and eventually occupy more than 90% of vehicle market.

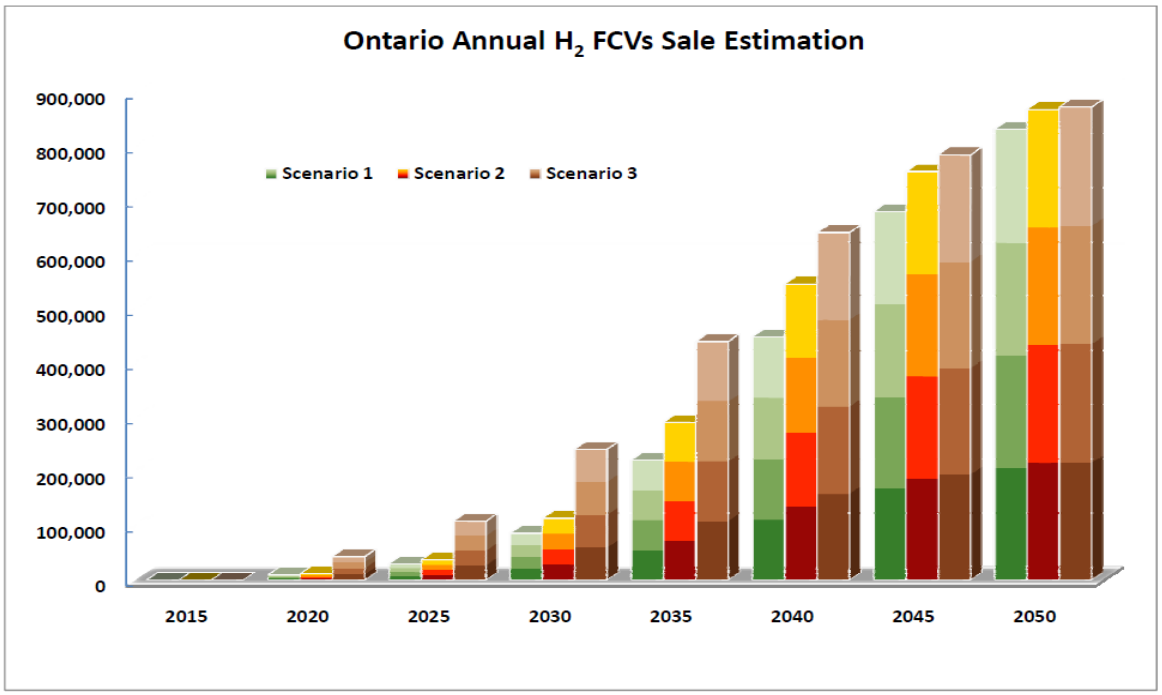


Figure 3.4: Ontario Annual H_2 FCVs Sale

3.2.2.4 Estimation of the accumulative number of H_2 FCVs in Ontario from 2015 to 2050

The total number of fuel cell vehicles was estimated by the following equation

$$Ni=N_{accumulation}-N_{unused\ car} \quad (3.4)$$

Where, $N_{accumulation}$ is the total number of H_2 FCVs sold from the 1st year to the i^{th} year

$N_{unused\ car}$ is the number of H_2 fuel cell vehicles which stop working from the 1st year to i^{th} year

N_i is the total number of H_2 fuel cell vehicles running on road in the year, i

Assume $N_{unused\ car}$ is the number of H_2 FCVs which are out of vehicle lifetime, and equation (3.4) is transformed as follows

$$Ni=N_{accumulation}-N_{Out\ of\ vehicle\ lifetime} \quad (3.5)$$

Where, $N_{out\ of\ vehicle\ lifetime}$ is the total number of H_2 FCVs beyond vehicle lifetime. $N_{out\ of\ vehicle\ lifetime}$ can be estimated to be the cumulative number of H_2 FCVs sold from the 1st year to the year of "i-lifetime". For example, if the vehicle lifetime is 10 year, and then $N_{out\ of\ vehicle\ lifetime}$ will be the cumulative number of H_2 FCVs sold from the 1st year to i-10th year. Thus, the next section is to estimate vehicle lifetime.

3.2.2.4.1 Fuel Cell Vehicles' Lifetime

Lifetime of a car was estimated by the equation below,

$$LT = LM/TD \quad (3.6)$$

Where, LT is average lifetime of vehicles in Ontario (year)

LM is average lifetime mileage of vehicles in Ontario (km)

TD is average annual travel distance of vehicles in Ontario (km/year)

Thus, to solve for lifetime of a vehicle, values of vehicle lifetime mileage LM and annual travel mileage TD must be found.

3.2.2.4.2 Vehicle Lifetime Mileage and Annual Travel Mileage

According to the report "vehicle survivability and travel mileage schedule" [62], the lifetime mileage of a passenger car was estimated to be 152137 miles. Since the cost of FCV is likely to be high it was assumed that FCV would be on the road at least as long as the current vehicles. This is likely a conservative estimate since a FCV power train has far fewer moving parts than the current internal combustion engines. One assumed this number was the value of LM, and the survey of Statistics Canada [63] also showed total travel distance of all vehicles in Ontario, 2005 was estimated to be 125101.7 million kilometres, while, in 2005, the number of registered vehicle in Ontario was 7,130,323. Substituting these two numbers into equation 3.7 shown below, one can estimate the average annual travel distance per vehicle, TD. Substitute TD into equation 3.6 and solve for LT, the average lifetime of Ontario's vehicle, which was calculated to be 14 years.

$$TD = TD_{total} / N_{registered\ vehicles} \quad (3.7)$$

Where, TD_{total} is total estimated travel distance of all vehicles in Ontario (km)

$N_{registered\ vehicles}$ is the number of registered vehicles in Ontario (vehicle)

So, upon the equation 3.7, solve equation 3.6 for LT with LM and TD, and use equation 3.2 to estimate the number of H_2 FCVs sold each year, and then apply equation 3.4 to achieve the total number of FCVs running on the road in Ontario. The estimation of total number of FCVs in Ontario was modeled in Simulink and illustrated in Figure A1-A3. Table 3.3 displays the estimated number of on-road H_2 FCVs in Ontario from 2015 to 2050. Once again it is felt that this a conservative estimate (i.e. assuming that FCV will last the same as current vehicles), but it is anticipated with improving technology that the durability of vehicles will increase overall.

Table 3.3: Total Estimated Number of on-road H_2 FCVs in Ontario from 2015 to 2050

Year	2015	2020	2025	2030	2035	2040	2045	2050
Scenario1, H_2 FCVs	0	32,336	132,070	423,990	1,179,800	2,816,700	5,410,800	8,347,700
Scenario2, H_2 FCVs	0	36,941	159,530	540,370	1,546,200	3,602,700	6,514,900	9,404,000
Scenario3, H_2 FCVs	0	152,760	543,690	1,432,700	3,032,500	5,383,400	7,988,200	10,202,000

As demonstrated in Figure 3.5, the number of hydrogen FCVs starts increasing in 2015 and increases sharply after FCVs market penetration in 2025. Finally the number reaches the peak in 2050 as hydrogen FCVs occupies major part of vehicle market.

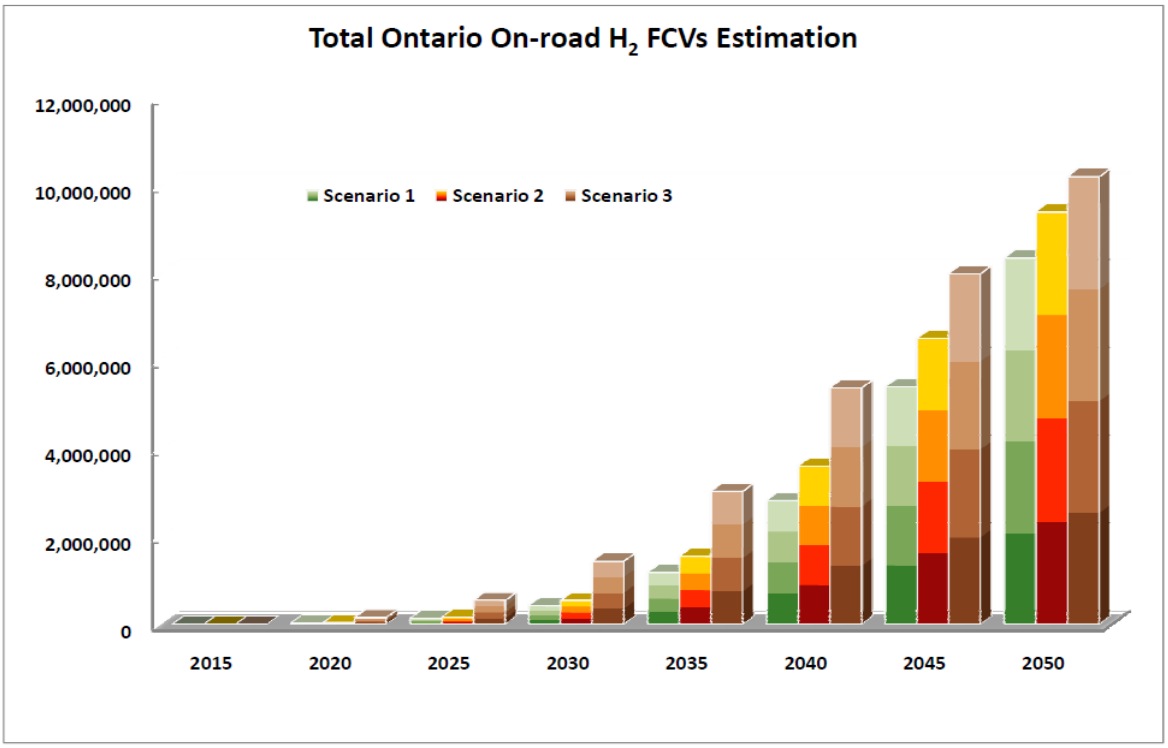


Figure 3.5: Total Number of Ontario On-road FCVs

3.2.3 Hydrogen Demand from all Hydrogen Fuel Cell Vehicles in Ontario

Based on the estimation of H_2 FCVs market development, one evaluated the resulting hydrogen demand. Firstly one estimated hydrogen consumption from a hydrogen fuel cell vehicle, and then multiplied the fuel consumption by the number of H_2 FCVs to derive hydrogen demand from all H_2 FCVs in Ontario.

3.2.3.1 Hydrogen Consumption of a Hydrogen Fuel Cell Vehicle

Currently there is still no fully commercial hydrogen fuel cell vehicle in the market yet, but relatively successful fuel cell vehicle demonstration models can be taken as a reference case, such as GM Equinox Fuel Cell Vehicle, which has been tested on a 100-fleet scale [64]. Note that this 100-fleet trial program is similar to that of Honda's for their clarity vehicles [65], but this work will use the Equinox for the model as it is a light sport utility vehicle, and as such it represents a worst case of high hydrogen vehicle demand. Fuel economy of this model is shown in Table 3.4.

Table 3.4: Equinox Fuel Cell Vehicle Specification Sheet [66]

Vehicle Style	Fuel Storage Type	Fuel Storage Pressure (bars)	Fuel Storage Capacity (kg)	Operating Range (km)
front-wheel drive SUV	carbon fiber fuel tank, compressed hydrogen gas	700	4.2	320

The model assumed that the GM Equinox fuel cell vehicle was the standard fuel cell vehicle, and assumed fuel economy of Equinox would be the average fuel consumption of H_2 FCVs. Thus hydrogen consumption per H_2 FCV was estimated as follows in equation 3.8 and 3.9.

H_{FCVs} = 4.2 kg hydrogen storage/ 320 km operating range =0.0131 kg H_2/ km (3.8)

Therefore, total hydrogen demand per H_2 FCV in a year was estimated by the equation below

$$HY_{FCVs} = H_{FCVs} \times TD \quad (3.9)$$

Where, HY_{FCVs} is average hydrogen demand of a hydrogen fuel cell vehicle in a year (kg H_2/

FCV. Year),

TD was given in equation 3.7.

3.2.3.2 Hydrogen Demand from all H_2 FCVs in Ontario

$$HT_{FCVs} = HY_{FCVs} \times Ni \quad (3.10)$$

Where, HT_{FCVs} is hydrogen demand from all H_2 FCVs in Ontario (kg H_2), shown in Table 3.5 and Figure 3.6. The estimation of hydrogen demand was modeled in Simulink as shown in Figure A3.

Table 3.5: Hydrogen Demand of H_2 FCVs in Ontario from 2015-2050

Year	2015	2020	2025	2030	2035	2040	2045	2050
Scenario 1, H_2 Demand (kg/year)	0	7.45E+06	3.04E+07	9.76E+07	2.72E+08	6.49E+08	1.25E+09	1.92E+09
Scenario 2, H_2 Demand (kg/year)	0	8.51E+06	3.67E+07	1.24E+08	3.56E+08	8.30E+08	1.50E+09	2.17E+09
Scenario 3, H_2 Demand (kg/year)	0	3.52E+07	1.25E+08	3.30E+08	6.98E+08	1.24E+09	1.84E+09	2.35E+09

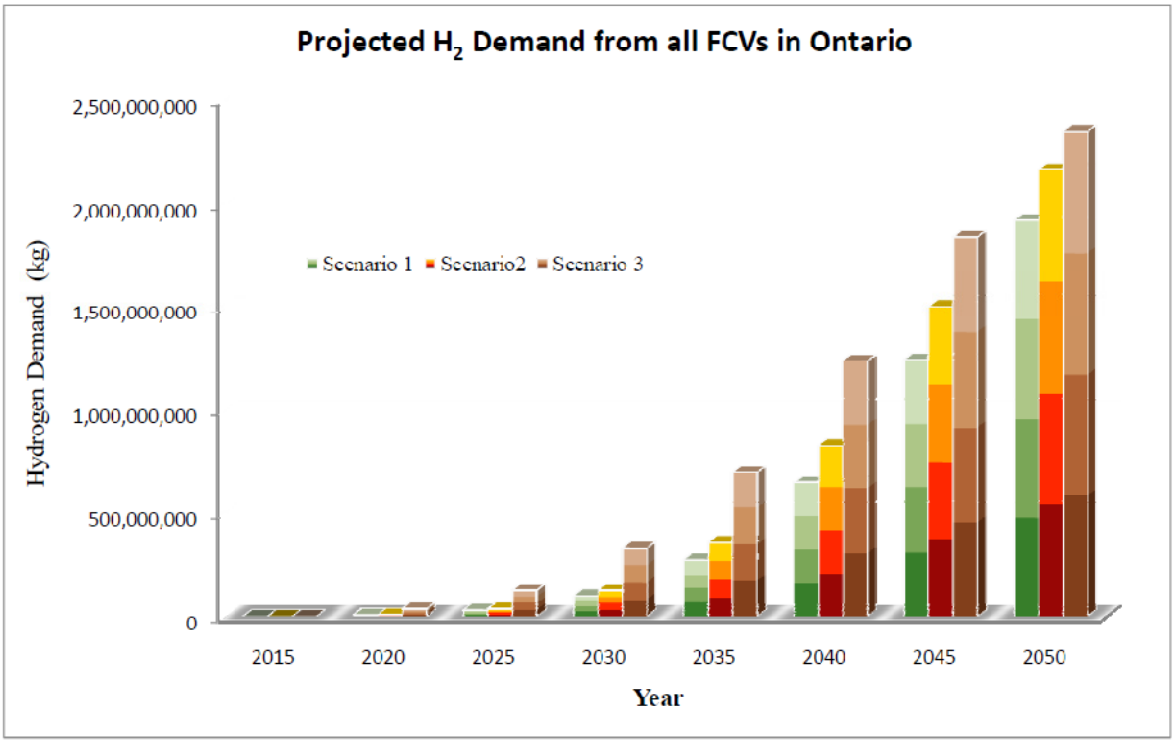


Figure 3.6: Total Hydrogen Demand from FCVs in Ontario

3.3 Hydrogen Pathway Analysis

In this section, an economic analysis for hydrogen production, storage and distribution was implemented to investigate hydrogen cost based on the estimated hydrogen demand of H_2 FCVs in Ontario. There are a few ways to produce hydrogen such as steam reforming of methane, water electrolysis, high temperature electrolysis, and thermochemical cycle hydrogen production. The selection of hydrogen production technology and distribution methods is different geographically due to regional limitations and energy generation capacity considered [67]. In Ontario there is a policy decision to eliminate energy production from coal in order to address climate change concerns, and thus hydrogen form coal was not assumed in this work, but others have considered coal [68]. In Ontario approximately 50% of power comes from nuclear and 25% from renewable energy resources with specific goals to increase renewable energy generation.

Steam reforming of methane is the most common process to produce hydrogen in large scale production at this time, but it was not taken into account in this chapter as well, due to a large amount of carbon dioxide being generated as a by-product, and in the future there will be expected increases in natural gas price which will make SMR less competitive. Theoretically, high temperature electrolysis and thermochemical cycle don't produce any pollutant or greenhouse gas directly. The efficiencies of high temperature electrolysis and thermochemical cycles were projected to reach up to 48% and 45% respectively [69] [70], but these two methods are still at the early phase of research, not fully applicable at this time. Should these technologies advance beyond the research stage, future analysis should certainly take this into account [33]. In the thesis, centralized water electrolysis was investigated as a hydrogen production method, as it can be coupled with any electricity generation source (e.g. hydro, wind, solar, nuclear), is carbon dioxide free and has been commercially proven for 50 years. As such electrolysis for the production of hydrogen is considered currently commercially viable as well as environmentally sustainable. Note that during the transition to a full hydrogen economy, distributed hydrogen production by siting electrolysers is likely to be applied to meet the demand rather than centralized production [71]. Figure 3.7 demonstrates the flow chart of centralized hydrogen production and distribution analysis.

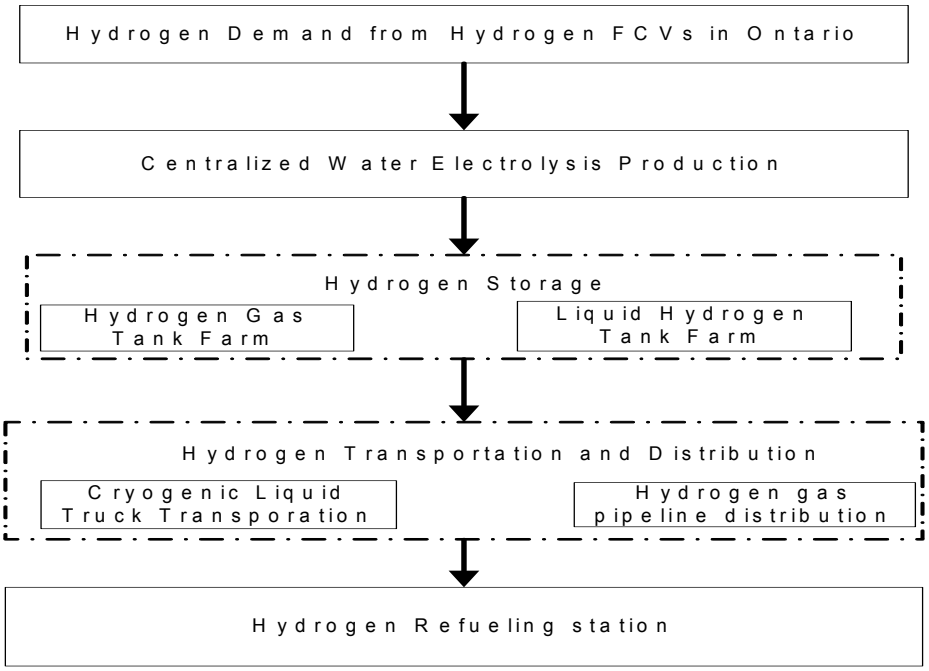


Figure 3.7: Flowchart of Hydrogen Cost Analysis

As shown in Figure 3.8, two hydrogen production and distribution pathways were investigated in this chapter. The first one is that hydrogen generated from centralized water electrolysis is first compressed, stored in high pressure storage tanks and then is distributed to the consumers through pipeline network. The second pathway is that generated hydrogen is liquefied, stored in cryogenic storage tanks, and finally is transported to the consumers by cryogenic trucks. These two pathways were modeled in Simulink as shown in Figure A4.

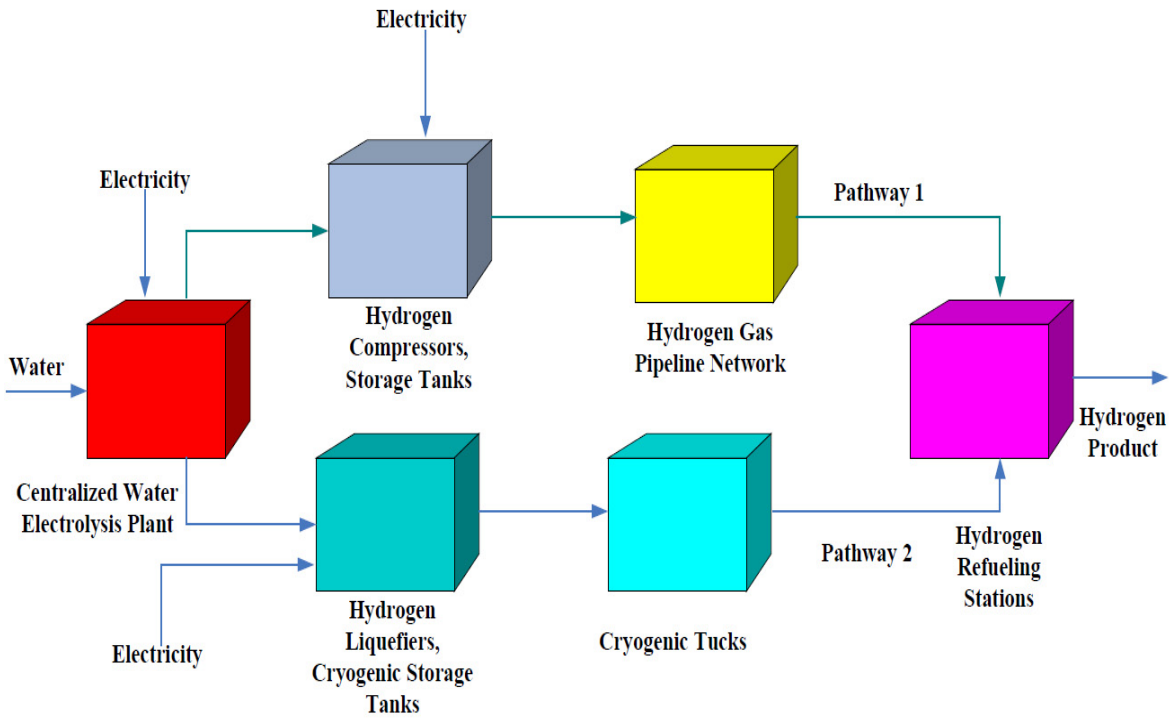


Figure 3.8: Centralized Water Electrolysis Hydrogen Production and Distribution Pathway

3.3.1 Cost of water electrolysis hydrogen production

In this chapter, as a preliminary economic analysis, cost of water electrolysis hydrogen production was considered to consist of two parts, operating cost and depreciable capital investment. Operating cost includes cost of water, electricity, labor and labor related costs while depreciable capital investment consists of some parts such as purchased equipment, piping, electrical, instrumentation and other costs. Table 3.6 demonstrates the assumptions of water electrolysis hydrogen production. Note that since that centralized hydrogen production was under consideration in this work, and it was assumed that the hydrogen production would be co-located (or very close) with primary energy production, and thus there was no electricity transmission cost added.

Table 3.6: Central Water Electrolysis Hydrogen Production Assumptions

Parameters	Assumption
Conversion Efficiency (water to hydrogen)	0.8[23]
Energy Efficiency (electricity to hydrogen)	0.73 [23]
Price of electricity (CAD/kWh)	0.05
Price of water (CAD/1000 litres)	1.29 [72]
Plant life (year)	30
Electrolyzer cell stack lifetime (year)	10 [23]
Progress ratio of electrolyzer hydrogen generation station	0.85 [73]
Price of electrolyzer hydrogen generation station (USD)	880,662 [73]
Capacity of electrolyzer hydrogen generation station unit (kg H_2/h, unit)	4.17
The number of shift operators (operators/shift)	4
Wage of operator (CAD/h)	35
Labor related cost (% labor cost)	60
Plant operating day	365
Assumed Inflation rate (%)	2.6
Currency Exchange Rate (USD/CAD)	0.845423
Depreciable Capital Investment Parameter [74]	
Piping (% of purchased equipment cost)	0.42
Electrical (% of purchased equipment cost)	0.12
Instrumentation (% of purchased equipment cost)	0.22
Foundation (% of purchased equipment cost)	0.1
Insulation (% of purchased equipment cost)	0.05
Painting, fireproofing and safety (% of purchased equipment cost)	0.06
Yard Improvement	0.1
Environmental	0.2
Building (% of purchased equipment cost)	0.52
Land (% of purchased equipment cost)	0.05
Utility Facility (% of purchased equipment cost)	0.52

3.3.1.1 Cost of Water Consumption

Water consumption was estimated by the equation below,

$$W_{consumption} = F_{hydrogen} \times M_{water} / (M_{hydrogen} \times \varepsilon_{conversion}) \quad (3.11)$$

Where, $W_{consumption}$ is water consumption by water electrolysis (kg H_2O/h)

$F_{hydrogen}$ is flow rate of hydrogen output (kg H_2/h)

M_{water} is molecular weight of water (kg H_2O/mol)

$M_{hydrogen}$ is molecular weight of hydrogen (kg H_2 /mol)

$\varepsilon_{conversion}$ is conversion efficiency of water to hydrogen (%)

Price of electricity shown in Table 6 was multiplied by $W_{consumption}$, and then one could achieve cost of water consumption.

3.3.1.2 Cost of Electricity Consumption

Consumption of electricity was defined as follows,

$$E_{consumption} = H_{heating\ value} \times F_{hydrogen} / \varepsilon_{energy} \quad (3.12)$$

Where, $E_{consumption}$ is electricity consumption of water electrolysis (kW)

$H_{heating\ value}$ is high heating value of hydrogen, 39kWh/kgH_2 [75].

ε_{energy} is energy efficiency of water electrolysis (%)

3.3.1.3 Labor Cost

Assuming 4 operators at a shift, the total cost of labor was calculated as follows,

$$L_{cost} = N_{operator} \times S_{operator} / F_{hydrogen} \quad (3.13)$$

Where, L_{cost} is labor cost (\$/kg H_2)

$N_{operator}$ is number of operators at a shift (operator)

$S_{operator}$ is wages of operators (\$/ h. operator)

3.3.1.4 Depreciable Capital Investment

3.3.1.4.1 Cost of Hydrogen Electrolyzers

Electrolyzer unit price was given in Table 3.6, but considering a large quantity of units required by centralized hydrogen production, electrolyzer unit price could decrease to some level. Progress ratio equations [76] were introduced to simulate the process of price being decreased.

$$SC = SC_0 \left(\frac{C}{C_0} \right)^{-b} \quad (3.14)$$

$$Pr = 2^{-b} \quad (3.15)$$

*W*here, SC is unit cost with cumulative capacity C

C is cumulative capacity

b is learning index (constant)

C_0 is initial cumulative capacity

SC_0 is initial unit cost with initial cumulative capacity

Pr is progress ratio

Cumulative capacity was defined as the total number of electrolyzer hydrogen generation station, while initial cumulative capacity C_0 is 1. Cost of electrolyzer generation station SC_0 and value of progress ratio Pr have been given in Table 3.6, and then one can achieve the unit cost SC and the total cost of electrolyzer hydrogen generation stations. The estimation of electrolyzer cost was modeled in Simulink as shown in Figure A5.

3.3.1.4.2 Plant Cost Estimating Factors

The total cost of plant was estimated by the factor method, assuming cost of other part of plant to be fractions of purchased equipment cost. Thus, the total cost of plant will become the multiplication of the sum of factors and cost of purchased equipments. Values of factors were shown in Table 3.6.

3.3.1.4.3 Depreciation of Total Plant Cost

As a preliminary economic analysis, the straight line method [77] was applied to calculate depreciation of total plant cost. Straight line calculation is shown as follows,

Depreciation = (Original plant cost –Salvage value)/ plant life time, years

Salvage value was assumed to be zero and value of plant lifetime is displayed in Table 3.6.

3.3.1.5 Cost of Electrolysis Hydrogen Generation

Upon estimation results achieved above, cost of electrolysis hydrogen generation was estimated

by the equation below and was modeled in Simulink as shown in Figure A6-8.

$$TCP = CP_{electricity} + CP_{water} + CP_{labor\ and\ related} + CP_{depreciation} \quad (3.16)$$

Where, TCP is total cost of electrolysis hydrogen generation ($/kg H_2)

$CP_{electricity}$ is unit cost of electricity consumption of electrolysis ($/kg H_2)

CP_{water} is unit cost of water consumption of electrolysis ($/kg H_2)

$CP_{labor\ and\ related}$ is unit cost of labor and related parts ($/kg H_2)

$CP_{depreciation}$ is unit depreciation from capital investment ($/kg H_2)

3.3.2 Cost of Compressed Gaseous Hydrogen Storage and Pipeline Distribution

3.3.2.1 Gaseous Hydrogen Storage

At this time the only commercialized storage methods in large scale are as a compressed gas or a liquid. Due to low gas storage density, compressing hydrogen gas prior to storage is considered to be an economical way to store hydrogen. The process of hydrogen gas storage requires high pressure compressors and storage tanks, thus cost of hydrogen storage will be derived from operating cost and capital investment of compression and storage equipments. Parameters and equations of hydrogen storage and pipeline distribution are shown in Table 3.7 and 3.8.

Table 3.7: Parameters of Gaseous Hydrogen Storage and Distribution [39] [74]

Parameter	Assumption
Operating pressure of hydrogen compressors, P (bar)	100
Base size of hydrogen compressor, CompSize(kW)	4000
Size exponent of hydrogen compressor, CompExp	0.8
Pressure exponent of hydrogen compressor, CpExp	0.18
Base pressure of hydrogen compressor, P_1 (bar)	200
Atmospheric pressure P_0 (bar)	1
Base power consumption of hydrogen compressor, ComPower (kWh/kg H_2)	2.2
Base cooling water consumption of hydrogen compressors, CompCool (gallon / kg H_2)	13.23
Base capital cost of hydrogen compressors, CompCost(USD/kW)	1000
Cost of cooling water (USD/1000gallon)	0.07
Hydrogen storage time (hr)	24
Hydrogen storage pressure, P (bar)	100
Base tank cost, TankCost (USD/kg H_2)	1323
Base tank size, TankSize (kg H_2/tank)	227
Base pressure of hydrogen storage tanks, TankPress(bar)	200
Size exponent of storage tanks, TankExp	0.75
Pressure exponent of storage tanks, TPExp	0.44
Capital Investment Parameter of gas tanks	
Piping (% of purchased equipment cost)	0.42
Electrical (% of purchased equipment cost)	0.12
Instrumentation (% of purchased equipment cost)	0.22
Foundation (% of purchased equipment cost)	0.1
Insulation (% of purchased equipment cost)	0.05
Painting, fireproofing and safety (% of purchased equipment cost)	0.06
Building (% of purchased equipment cost)	0.05

Table 3.8: Equations of Gaseous Hydrogen Storage and Distribution [39] [78]

$$E_{compr} = Flow \bullet ComPower \bullet \left[\frac{\ln\left(\frac{P}{P_0}\right)}{\ln\left(\frac{P_1}{P_0}\right)} \right] \quad (3.17)$$

E_{compr} is power consumption of high pressure hydrogen compressors (kWh/h)

$$Cooling = Flow \bullet CompCool \bullet \left[\frac{\ln(\frac{p}{P_0})}{\ln(\frac{P_1}{P_0})} \right] \quad (3.18)$$

Where, Cooling is cooling water consumption of high pressure hydrogen compressors (gallon/h)

$$CompCap = (CompCost \bullet CompSize) \bullet \left(\frac{E_{compr}}{CompSize} \right)^{CompExp} \bullet \left(\frac{P}{p_1} \right)^{CpExp} \quad (3.19)$$

Where, CompCap is cost of high pressure hydrogen compressors (USD)

$$TankCap = (TankCost \bullet TankSize) \bullet \left(\frac{Storage \bullet \frac{Tank\ \mathrm{Pr}ess}{P}}{TankSize} \right)^{TankExp} \bullet \left(\frac{P}{Tank\ \mathrm{Pr}ess} \right)^{TPExp} \quad (3.20)$$

Where, Tank Cap is cost of hydrogen storage tanks (USD)

H_2 Pipeline Cost = $[0.9597D^2 + 492.06D+418790]$ L + 378750 (3.21)

Where, D is the diameter of hydrogen gas pipeline (meter), and L is distance(km)

3.3.2.1.1 Operating Cost of Hydrogen Compression

Hydrogen compressors consume power and cooling water, therefore operating cost of hydrogen storage will be derived from cost of power and cooling water consumption estimated by equation 3.17 and 3.18. Since storage tanks are usually integrated with production site, production and storage facilities are always operated together, and thus cost of labour and the related costs for hydrogen storage are not counted separately in this analysis.

3.3.2.1.2 Depreciable Capital Investment

As mentioned in the previous section, high pressure hydrogen compressors and gas tanks are the main equipments for hydrogen gas storage, and costs of compressors and compressed gas tanks were estimated by equation 3.19 and 3.20 respectively. The total cost of gaseous storage tanks was estimated by the factor method, and compressors and storage tanks were regarded as the main purchased equipment. Value of purchased equipment factor was considered to be 1.00, while values of other factors were assumed to be a fraction of the main equipment shown in Table 3.7. Depreciation was calculated by straight line method, same as section 3.3.1.2.2.

3.3.2.1.3 Total Cost of Gaseous Hydrogen Storage

Total cost of gaseous hydrogen storage was computed as follows and modeled as shown in Figure A9-12.

$$TCS = CS_{electricity} + CS_{cooling\ water} + CS_{depreciation} \quad (3.22)$$

Where, TCS is total cost of gaseous hydrogen storage ($/kg H_2)

$CS_{electricity}$ is unit cost of energy consumption from compression ($/kg H_2)

$CS_{cooling\ water}$ is unit cost of cooling water consumption from compression ($/kg H_2)

$CS_{depreciation}$ is unit depreciable hydrogen gas storage capital investment ($/kg H_2)

3.3.2.2 Hydrogen Gas Pipeline Distribution

Capital investment of hydrogen gas pipeline was estimated by equation 3.21 [78] and was modeled as shown in Figure A13. The length of the pipeline was assumed to be 200 km which is approximately the distance from Bruce Nuclear Power Plant to the Great Toronto Area (GTA) where most of the hydrogen demand would be located.

3.3.3 Cost of Liquid Hydrogen Storage and Transportation

Parameters, assumptions and equations are demonstrated in Table 3.9 and 3.10.

Table 3.9: Parameters of Liquid Hydrogen Storage [39]

Parameter	Assumption
Unit power consumption of hydrogen liquefiers, LiqPower (kWh/kg H_2)	9.921
Unit cooling water consumption of hydrogen liquefiers, LiqCool (gallon/kg H_2)	165.34
Base size of hydrogen liquefiers, LiqSize (kg H_2/h)	453.6
Unit Cost of liquefiers, LiqCost (USD, h/kg H_2)	44092
Base size of liquid hydrogen storage, StorageSize (kg H_2)	45.36
Unit cost of liquid hydrogen storage, StorageCost (USD/kg H_2)	441
Boil-off rate of liquid hydrogen storage (%)	0.1
Size exponent of hydrogen liquefiers, LiqExp	0.65
Size exponent of hydrogen storage tanks, DewarExp	0.71
Depreciable capital investment factors of liquid hydrogen storage	
Piping (% of purchased storage equipment cost)	0.42
Electrical (% of purchased storage equipment cost)	0.12
Instrumentation (% of purchased storage equipment cost)	0.22
Foundation (% of purchased storage equipment cost)	0.1
Insulation (% of purchased storage equipment cost)	0.05
Painting, fireproof, painting (% of purchased storage equipment cost)	0.06
Building (% of purchased storage equipment cost)	0.05
Cost of a liquid hydrogen truck trailer, TrailerPrice (USD)	350000
Cost of a liquid hydrogen truck undercarriage, UnderPrice (USD)	60000
Cost of a liquid hydrogen truck cab, CabPrice (USD)	90000
Size of liquid hydrogen truck trailer (kg H_2)	4082
life time of trailer and undercarriage (year)	10
life time of cab (year)	15
Transportation distance (km)	200
Hydrogen boil-off rate (%)	0.3
Price of truck fuel (USD/gallon)	2.45
Fuel economy of truck (km/gallon)	9.656
Driver wage (USD/h)	30
Truck availability (h/d)	24
Truck speed (km/h)	80
Load time (h)	1
Unload time (h)	1

Table 3.10: Equations of Liquid Hydrogen Storage [39]

$Energy = Flow \bullet LiqPower$	(3.23)
Where, Energy is power consumption of hydrogen liquefiers (kWh/h)	
$Cooling = Flow \bullet LiqCool$	(3.24)
Where, cooling is the cooling water consumption of hydrogen liquefiers (gallon/h)	
$LiqCap = (LiqCost \bullet LiqSize)\left(\frac{Flow}{LiqSize}\right)^{LiqExp}$	(3.25)
Where, LiqCap is cost of liquefiers (USD)	
$StorageCap = (StorageCost \bullet StorageSize)\left(\frac{Storage}{StorageSize}\right)^{DewarExp}$	(3.26)
Where, StorageCap is cost of liquid hydrogen storage (USD)	
$TruckCap = TruckNumber\ (CabPrice + TrailerPrice + UnderPrice)$	(3.27)
Where, TruckCap is capital cost of a cryogenic tank trucks TruckNumber is the number of tank trucks needed for liquid H_2 transportation	
$LaborCosts = TranspHours \times DriverWage$	(3.28)
Where, TranspHours are the hours of liquid hydrogen transportation	
$FuelCost = DieselOilPrice \times TruckMileage$	(3.29)

3.3.3.1 Cost of Liquid Hydrogen Storage

The principal alternative to compressed hydrogen is liquefied hydrogen. Liquefiers and cryogenic storage tanks are required in hydrogen liquefaction process. Consequently, cost of liquid hydrogen storage was considered to be the sum of operating cost of liquefaction process, storage and depreciation of capital investment. Operating cost consists of power consumption, cooling water consumption, and labor cost. For the same reason described in section 3.3.2.1.1, labor cost was not taken into consideration of liquid storage. Power and cooling water consumption were evaluated by equation 3.22 and 3.23 respectively. Cost of liquefiers and cryogenic storage tanks

were the main parts of capital investments, while costs of other parts were assessed by factor method. Factor values were given in Table 3.9.

3.3.3.2 Cost of Cryogenic Truck Transportation

Cost of cryogenic truck transportation was considered to consist of truck fuel cost, labor cost and cost of cryogenic trucks. These three parts were estimated by equation 3.27, 3.28 and 3.29 in Table 3.10.

The estimation of cost of liquid hydrogen storage and transportation was modeled in Simulink as show in Figure A14-19.

3.3.4 Cost of Hydrogen

Combining all parts from production to distribution, one estimated the total cost of liquid and gaseous hydrogen from production, storage to distribution. Tables 3.11 and 3.12 illustrate cost of liquid and gaseous hydrogen respectively. Costs of hydrogen of the three scenarios are different from each other due to different estimated hydrogen demand from the scenarios. Assume hydrogen demand of each scenario can be met by hydrogen electrolysis production each year, and then the amount of demand becomes hydrogen electrolysis production capacity. As shown in results, larger scale production can generate lower unit cost of product. However, the results also show that when production scale is increased up to some level, impact of production scale will become very small, and costs of hydrogen of the three scenarios turns to be almost identical.

As shown in Table 3.11 cost of gaseous hydrogen for each scenario is relatively high in 2015 because of low capacity of water electrolysis production, but after the transition period, hydrogen demand from FCVs in Ontario starts growing rapidly as the market expands, and hydrogen production capacity is also increasing to meet hydrogen demand. The unit cost of hydrogen generation stations starts to drop as more electrolysis units are purchased and the technology of

hydrogen generation become more mature. Meanwhile, since hydrogen production capacity increases significantly, the unit cost from capital investment of infrastructural facilities such as storage tanks and pipelines also decrease due to impact of economies of scale, so overall the cost of hydrogen starts to drop and eventually cost of hydrogen decreases to about 3$/kg H_2 in 2050.

Table 3.11: Cost of Gaseous Hydrogen versus Hydrogen Demand

	Scenario 1		Scenario 2		Scenario 3	
Year	hydrogen demand kg/year	Cost of gaseous hydrogen $/kg	hydrogen demand kg/year	Cost of gaseous hydrogen $/kg	hydrogen demand kg/year	Cost of gaseous hydrogen $/kg
2016	8.97E+05	8.40	9.87E+05	8.05	4.59E+06	4.89
2020	7.45E+06	4.46	8.51E+06	4.37	3.52E+07	3.76
2025	3.04E+07	3.81	3.67E+07	3.75	1.25E+08	3.49
2030	9.76E+07	3.54	1.24E+08	3.50	3.30E+08	3.36
2035	2.72E+08	3.38	3.56E+08	3.35	6.98E+08	3.28
2040	6.49E+08	3.29	8.30E+08	3.26	1.24E+09	3.23
2045	1.25E+09	3.23	1.50E+09	3.21	1.84E+09	3.20
2050	1.92E+09	3.19	2.17E+09	3.19	2.35E+09	3.18

Cost of liquid hydrogen follows a similar tend as shown in Table 3.12; cost is high at the beginning period, starts dropping as the market expands, and finally reaches the bottom in 2050. However because of higher energy consumption from hydrogen liquefaction, liquid hydrogen product is still higher than gaseous hydrogen.

Table 3.12: Cost of Liquid Hydrogen versus Hydrogen Demand

	Scenario 1		Scenario 2		Scenario 3	
	hydrogen demand	Cost of liquid hydrogen	hydrogen demand	Cost of liquid hydrogen	hydrogen demand	Cost of liquid hydrogen
Year	kg/year	$/kg	kg/year	$/kg	kg/year	$/kg
2016	8.97E+05	8.05	9.87E+05	7.80	4.59E+06	5.33
2020	7.45E+06	4.97	8.51E+06	4.89	3.52E+07	4.30
2025	3.04E+07	4.35	3.67E+07	4.29	1.25E+08	4.01
2030	9.76E+07	4.06	1.24E+08	4.01	3.30E+08	3.86
2035	2.72E+08	3.89	3.56E+08	3.85	6.98E+08	3.77
2040	6.49E+08	3.78	8.30E+08	3.75	1.24E+09	3.71
2045	1.25E+09	3.71	1.50E+09	3.70	1.84E+09	3.68
2050	1.92E+09	3.68	2.17E+09	3.67	2.35E+09	3.66

The model shows that in the early years, costs of gaseous hydrogen storage and distribution are higher than liquid hydrogen storage and transportation. It is because that initially gaseous hydrogen storage and distribution need much greater capital investment to build storage facilities and pipeline network than liquid hydrogen storage and transportation, which only need a number of storage tanks and trucks. Meanwhile, only low capacity of hydrogen production is required to meet the demand from small fleet of FCVs in Ontario, and it causes overall cost of gaseous hydrogen greater than liquid hydrogen. However, when hydrogen fuel cell vehicle market expands, the production capacity is increasing as well. The unit cost of gaseous hydrogen storage and distribution is dropping more quickly than liquid hydrogen, and after FCVs market penetration cost of gaseous hydrogen storage and distribution become lower than liquid hydrogen product.

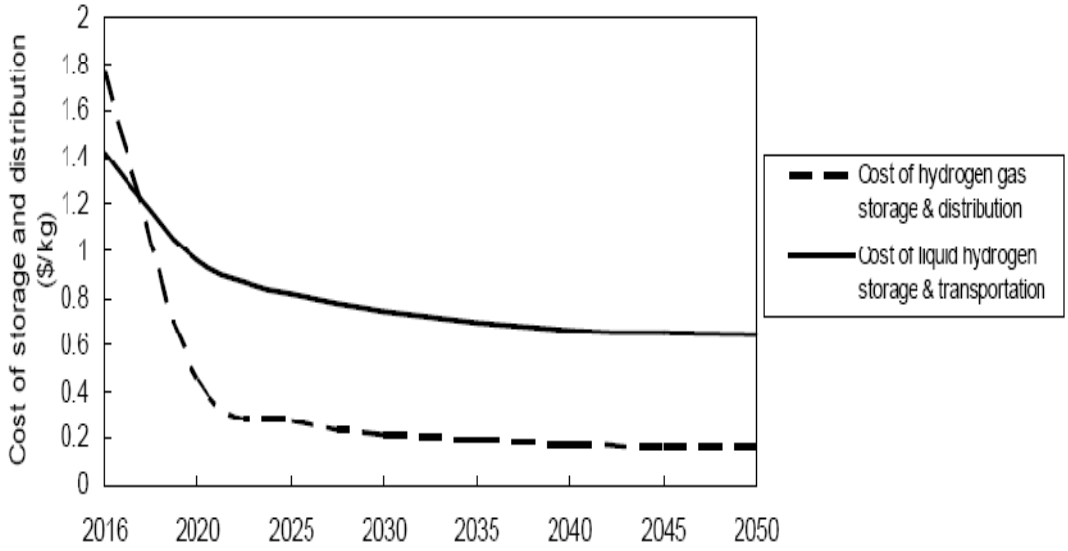


Figure 3.9: Cost of Hydrogen Storage and Distribution (Scenario 1)

From the discussion above and as shown in Figure 3.9, liquid hydrogen storage and distribution are suitable for small scale of hydrogen production during the transition period to a hydrogen economy while gas tank storage and pipeline distribution are preferable for large scale production as FCVs market is mature.

3.4 Sensitivity analysis

In the previous section, one discussed cost of hydrogen production from production to distribution. In this section, uncertainties of parameters such as price of electricity, price of water, energy efficiency of water electrolysis, and plant life are investigated.

Since electrolysis is a highly power consumed reaction, cost of hydrogen is highly sensitive to price of electricity. The model shows that, for scenario 1, based on the estimated hydrogen demand of 2016, when electricity price increases from 5 cents/ kWh to 7 cents/kWh, cost of gaseous hydrogen increases from 8.40$/kg to 9.55$/kg, Moreover, another 2 cents of electricity price increment makes cost of gaseous hydrogen become 10.69$/kg. Figure 3.10 demonstrates the impact of electricity price. Similar results are also achieved in liquid hydrogen analysis.

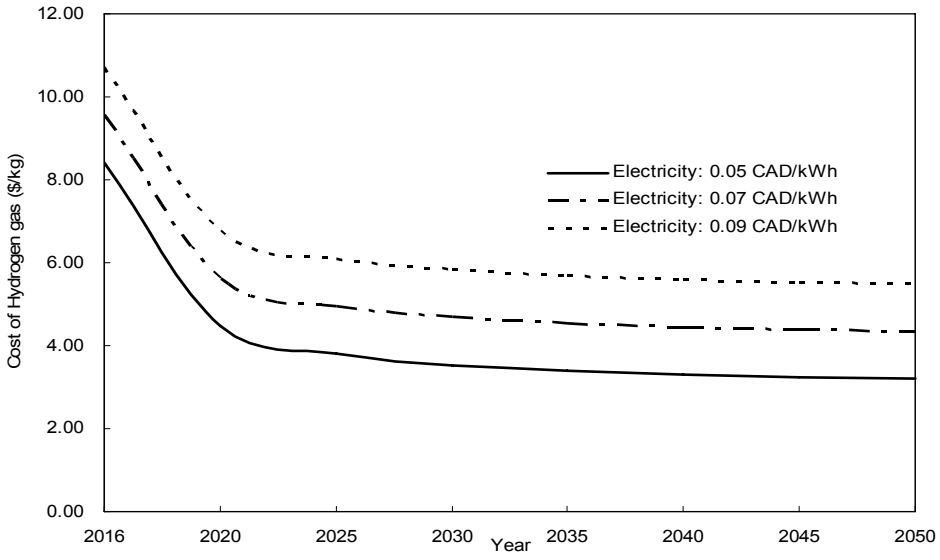


Figure 3.10: Electricity Price vs. Cost of Hydrogen gas of Scenario 1

Impact of water price is very little as shown in Table 3.13. Fluctuation of water price doesn't make any big difference on either liquid hydrogen or gaseous hydrogen. It is mainly because of low water price, over 1 dollar per cubic meter. However, one should notice that in the future when hydrogen demand becomes huge, price of water may increase dramatically and then the conclusion may be changed.

Table 3.13: Water Price vs. Cost of Hydrogen (Scenario 1)

	Water: 1.19$/m3		Water: 1.29$/m3		Water: 1.39$/m3	
Year	cost of gaseous hydrogen ($/kg H_2)	cost of liquid hydrogen ($/kg H_2)	cost of gaseous hydrogen ($/kg H_2)	cost of liquid hydrogen ($/kg H_2)	cost of gaseous hydrogen ($/kg H_2)	cost of liquid hydrogen ($/kg H_2)
2016	8.397	8.051	8.398	8.052	8.399	8.053
2020	4.460	4.971	4.462	4.973	4.463	4.974
2025	3.808	4.347	3.809	4.348	3.810	4.349
2030	3.536	4.059	3.537	4.061	3.539	4.062
2035	3.382	3.888	3.383	3.889	3.385	3.890
2040	3.285	3.779	3.287	3.780	3.288	3.781
2045	3.227	3.713	3.228	3.714	3.229	3.716
2050	3.193	3.676	3.194	3.677	3.196	3.678

Impact of electrolysis energy efficiency is insignificant. The model shows that two percentage of efficiency increment only obtains approximate 0.1$/kg decrease on cost of hydrogen. Table 3.14 shows how cost of gaseous hydrogen changes according to change of electrolysis energy efficiency.

Table 3.14: Energy Efficiency of Electrolysis vs. Cost of gaseous hydrogen (Scenario1)

Year	Efficiency: 70% cost of gaseous hydrogen ($/kg H_2)	Efficiency: 73% cost of gaseous hydrogen ($/kg H_2)	Efficiency: 76% cost of gaseous hydrogen ($/kg H_2)	Efficiency: 79% cost of gaseous hydrogen ($/kg H_2)
2016	8.52	8.40	8.29	8.19
2020	4.58	4.46	4.35	4.25
2025	3.93	3.81	3.70	3.60
2030	3.66	3.54	3.43	3.33
2035	3.50	3.38	3.27	3.17
2040	3.40	3.29	3.18	3.08
2045	3.35	3.23	3.12	3.02
2050	3.31	3.19	3.09	2.99

Lifetime of plant can make some influence on cost of hydrogen. Short lifetime of plant will generate large value of capital investment depreciation. The impact of plant lifetime is obvious in the early period when hydrogen production scale is small. However, when production scale is large enough, the impact of lifetime on the cost of hydrogen becomes weak. Figure 3.11 illustrates cost of gaseous hydrogen with different plant lifetime.

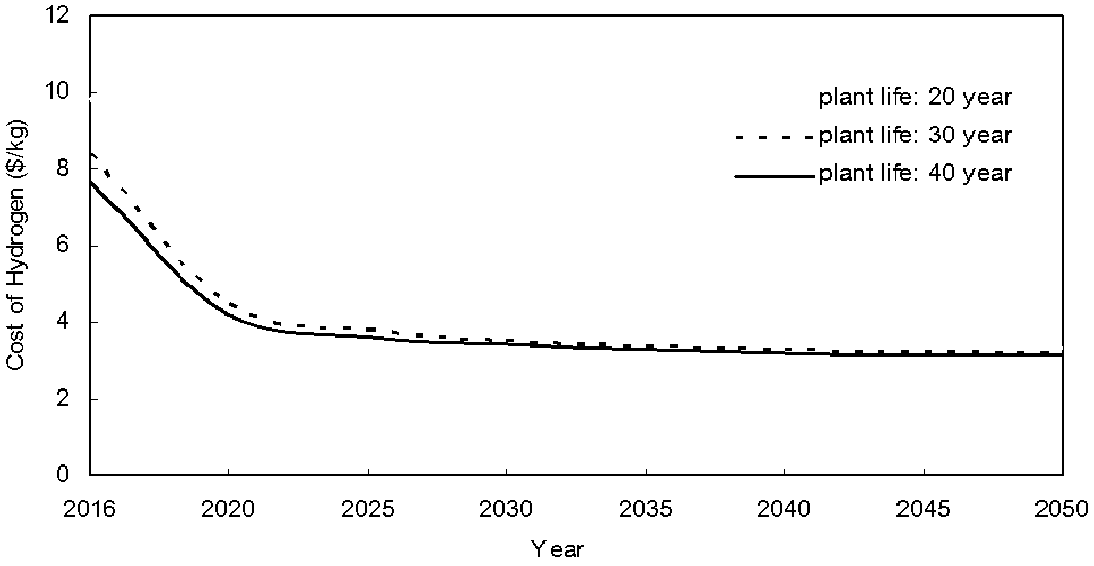


Figure 3.11: Plant Life vs. Cost of Hydrogen gas

3.5 Conclusions

In the chapter, logistic models were applied to represent fuel cell vehicle market penetration in Ontario, and three scenarios were established to demonstrate optimistic, moderate and conservative FCVs market development respectively. The number of FCVs and the corresponding hydrogen demand were estimated in the model. Based on demand estimation, costs of centralized water electrolysis hydrogen production, hydrogen storage and distribution were investigated. The analysis shows that

- According to the FCVs market penetration scenarios, hydrogen fuel cell vehicles enter the market in 2015, start market penetration in 2025, and occupy the major market in 2050. For scenario 1, 2 and 3, it was projected that there would be about 8.35, 9.40 and 10.2 million FCVs respectively in Ontario by the end of 2050, and hydrogen demand from all fuel cell vehicles in Ontario would be 1.92×10^9, $2.17\times10^9$and 2.3510^9kg H_2/year respectively.

- Based on the FCVs market penetration scenarios, cost of gaseous hydrogen generated by centralized water electrolysis via compressed gas pipeline to the GTA region in year of 2050 was estimated to be about 3.19$/kg, while cost of liquid hydrogen generated by centralized water electrolysis via cryogenic truck transportation was about 3.68$/kg.
- According to the hydrogen cost estimations, cost of gaseous hydrogen starts to level off at 3.81$/kg in 2025 for scenario1, 3.75$/kg in 2025 for scenario2, and 3.76$/kg in 2020 for scenario 3. Cost of liquid hydrogen starts to level off at 4.35$/kg in 2025 for scenario1, 4.29$/kg in 2025 for scenario 2 and 4.30$/kg for scenario3. It is mainly because that unit price of electrolysis station starts to drop as more units are purchased and the technology is more mature and less expensive, meanwhile the expenditure contributed to unit cost of hydrogen from infrastructural facilities like storage tanks and pipeline starts to decrease when hydrogen production capacity increases dramatically. And this is the time when large scale centralized hydrogen project will be mostly required.
- According to the sensitivity analysis, cost of hydrogen is very sensitive to price of electricity as electricity is the only energy consumed by water electrolysis and a small increment of electricity price can cause significant cost increase of hydrogen. Impact of water price is small at the current water price, but it may change when water consumption from electrolysis becomes huge and causes significant water price increase. Impact of plant life time on cost of hydrogen is obvious for small scale hydrogen production as shorter plant lifetime can cause greater depreciation and expenditure from capital investment to be contributed to unit cost of hydrogen. Impact of electrolysis efficiency is moderate on cost of hydrogen and 2% of efficiency increase can cause 0.1$/kg increase.

- The analysis also shows that pipeline distribution from centralized facilities is preferable for large scale hydrogen productions while cryogenic truck transportation is suitable for smaller scale production.
- For the conservative case of market penetration of hydrogen FCVs, scenario 1, total amount of hydrogen production demand from the fleet of light duty hydrogen vehicles is about 1.92×10^{9} kg /year in 2050, assuming that hydrogen production is wholly from water electrolysis and production capacity matches hydrogen demand exactly; power consumption from hydrogen production will be about 12140 MW and 13900 MW for gaseous and liquefied hydrogen respectively, which are about 36 % and 41% expansion of the current Ontario installed power generation capacity, 33770 MW [79].

Chapter 4

The Thermochemical Sulfur-Iodine Cycle Hydrogen Production

4.1 Considerations of Thermochemical Cycles

This work has focused on the centralized production of hydrogen, and in particular the centralized production of hydrogen at a nuclear site. Nuclear energy is particular receptive to the centralized production of hydrogen because it is a carbon dioxide free generation method, and has the capacity of production of the large quantities of electricity required for the generation of the required hydrogen. The analysis to this point has focused on the use of electrolysis as it is commercially proven technology. However, the use of thermochemical production of hydrogen in a centralized location coupled with nuclear power offers the potential for even greater efficiency. Also electrolysis and thermochemical decomposition of water applied in tandem with nuclear energy have a promising potential to generate hydrogen and electricity without leading to greenhouse gas emissions. Together they have a unique potential to serve both de-centralized hydrogen (electrolysis) needs in periods of low-demand electricity, and centralized base-load production from a nuclear station. Thermochemical methods have a significantly higher efficiency, but electrolysis can take advantage of low electricity prices during off-peak hours. By effectively linking these systems, emissions, productions of hydrogen can become more competitive against the predominant existing technology, SMR (steam methane reforming).

The development of thermochemical cycles is not well advanced to include a complete cycle analysis in this work, so this work has focused on the optimization of a section of this process (specifically the thermal management of a cycle), as well as qualitative introduction to a promising thermochemical cycle.

4.2 Introduction of Thermochemical S-I Cycle

The S-I Cycle was first invented at General Atomics in 1970s. Now, it becomes a promising hydrogen generation method [80]. Some studies show that the efficiency of S-I cycle can be over 40% [81], and through some process optimizations the efficiency might be projected to be over 60% [82]. Many research institutions have already started their studies on the thermochemical hydrogen production cycles coupled with the nuclear reactors [83-85].

Compared with other methods such as water electrolysis and high temperature electrolysis, thermochemical cycles have the potential to be the most efficient method for hydrogen production [86-89], This high efficiency is due to fact that there are no losses associated with electricity generation steps, and that thermal energy is converted directly to electrical energy. This process is still very much in the research development phase and the expectation of high efficiency need to be verified experimentally.

As discussed in Chapter 2, The Sulfur-Iodine Cycle consists of three reactions, Bunsen reaction, sulfuric acid decomposition and hydrogen iodide decomposition reactions. The reactions are shown as follows [90]

$I_2+SO_2+2H_2O \rightarrow 2HI+H_2SO_4$ (120℃)

$H_2SO_4 \rightarrow 1/2O_2+SO_2+H_2O$ (850℃)

$2HI \rightarrow H_2+ I_2$ (450℃)

Net reaction: $2H_2O \rightarrow 2H_2 +O_2$

As illustrated in Figure 4.1, Bunsen reaction is the central reaction of the cycle to produce sulfuric acid and hydrogen iodide. Oxygen is produced in sulfuric acid decomposition, whereas hydrogen is produced in hydrogen iodide decomposition. Sulfur dioxide and iodine from decomposition of hydrogen iodide and sulfuric acid are fed back to Bunsen reaction.

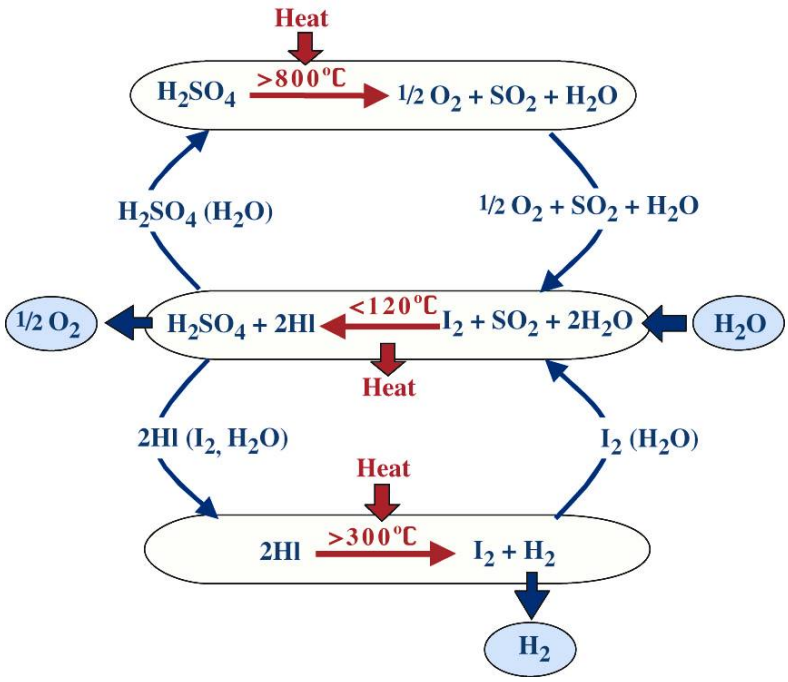


Figure 4.1: Sulfur-Iodine Cycle [91]

4.3 Conceptual Design of S-I Cycle

As shown in Figure 4.2, sulfuric acid and hydrogen iodide are produced by Bunsen reaction in Section I.

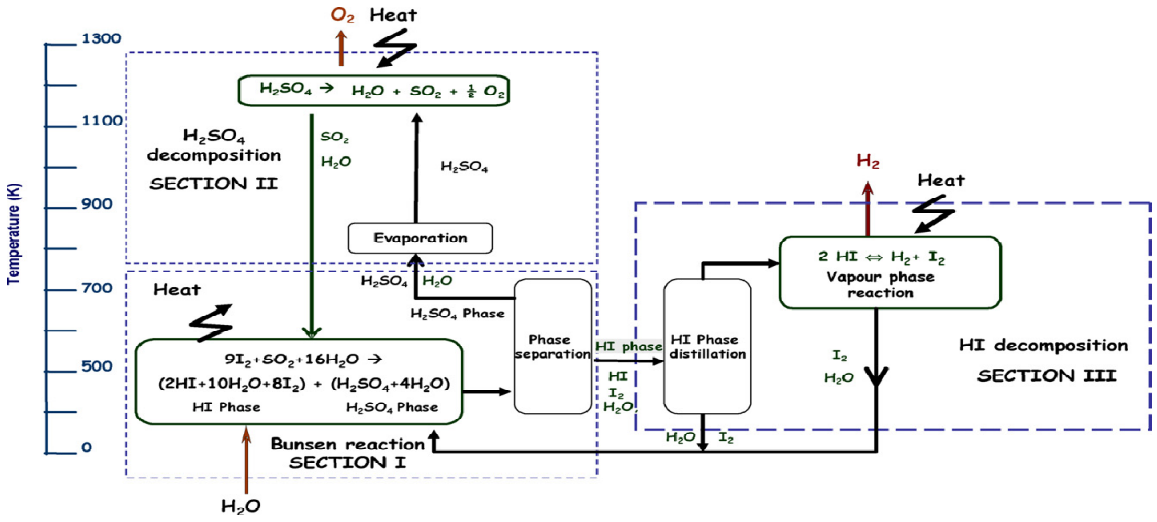


Figure 4.2: Conceptual Design of Sulfur-Iodine Cycle [92]

The resulting mixture of H_2SO_4 and HI is transferred into a phase separator. With the addition of

excessive iodine, sulfuric acid and hydrogen iodide are separated from each other. Sulfuric acid at the upper part of the phase separator is fed to section II, while HI at the bottom of the separator is transferred to the section III.

In section II, the sulfuric acid solution is concentrated by preheating and vaporization, and then is decomposed into SO_2, H_2O and O_2. SO_2 and H_2O are sent back to the Bunsen reaction, while O_2 is vented to the air or can be extracted as a by-product. In section III, HI is separated from the mixture of HI and I_2, and then is decomposed into H_2 and I_2 in the reactive distillation column. H_2 is extracted as a product, while I_2 is reused into Section I.

Thermochemical cycles are all conducted at high temperature. Therefore the efficiency of the reactions mainly relies on the availability of heat. Through exchanger network heat integration, a large amount of heat can be saved and the efficiency of reaction can be increased. In this chapter, heat integration is implemented in section II, because most of the heat in S-I cycle is consumed in this section.

4.4 Heat Integration of Sulfuric Acid Decomposition Process

As mentioned in the previous section, the energy of S-I cycle is wholly from the high temperature heat, so the way to utilize the heat will affect the overall efficiency of thermochemical cycle significantly, thus the optimization of heat exchanger network will be crucial for the S-I cycle production. The report [93] published by General Atomics demonstrated the preliminary process design of S-I cycle production and the heat integration will be developed upon the data from the decomposition process of sulfuric acid as the sulfuric acid decomposition is the most heat-consuming process in the cycle.

4.4.1 Description of Sulfuric Acid Decomposition

As illustrated in Figure 4.3, the sulfuric acid is first concentrated in a high pressure four-stage

isobaric concentrator.

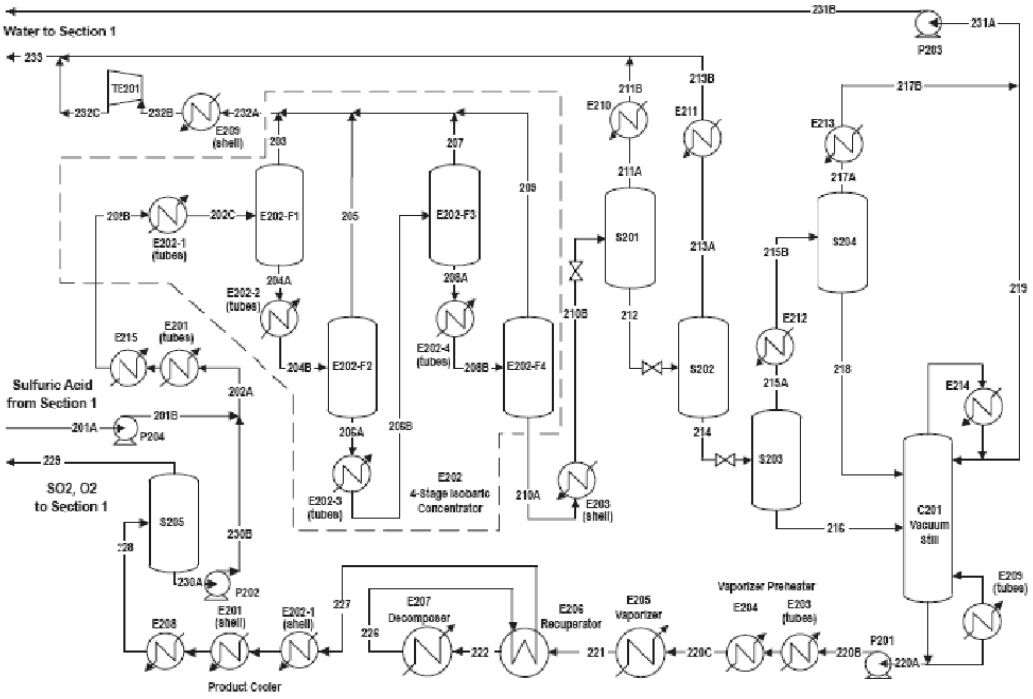


Figure 4.3: Flowsheet of Sulfuric Acid Decomposition Process [93]

At each stage, the sulfuric acid is heated and water is boiled off. After that, the acid gets further concentrated in a set of three flash tanks and a vacuum distillation column. Thus, the sulfuric acid is highly concentrated and is ready for the decomposition process. Prior to entering the decomposer, H_2SO_4 is preheated and evaporated at the specific temperature by a series of heat exchangers. In the decomposer, H_2SO_4 is split into SO_2, O_2 and H_2O. SO_2 and H_2O are sent back to the Bunsen reaction. Some parts of O_2 will be used as a carrier gas, and the rest will be vented to the air or sent for further purification.

4.4.2 Principles of Heat integration

The integration of heat exchangers network can be implemented as the following steps [77]

- Heat Duty Data Collection
- Select a minimum approach temperature

- Build a heat cascade diagram
- Set a transshipment model to minimize utility consumption
- Expand the transshipment model
- Add logical constraints to minimize the number of heat exchangers

4.4.3 Heat Duty Data Collection

Before the heat integration, the data (such as heat content, and temperature range of each process stream) should be collected. Vacuum still C201 is crucial to sulfuric acid decomposition process. The bottom distillation output is fed to sulfuric acid decomposer. The composition of vacuum distillation output has significant influence on sulfuric acid decomposition reaction. Independent utility supplies to reboiler E209 and condenser E214 can be advantageous to maintain composition of vacuum distillation output. So, optimal synthesis of the heat exchanger network excludes reboiler E209 and condenser E214. Based on the data in the report [65], all the material streams, excluding the streams of E209 and E214, are categorized as cold or hot streams. The corresponding heat duty data and temperature ranges are listed in Table 4.1.

Table 4.1: Heat Duty Data of Hot and Cold Streams [93]

Stream No.	Heat Content (kW)	Temperature Range (°C)	ΔT (°C)	Fcp (kW/°C)
Cold stream1		120.98		
Total Heat	193.542	330.15	209.17	0.925285653
Cold Stream2		330.15		
Total Heat	46.387	346.15	16	2.8991875
Cold Stream3		346.15		
Total Heat	29.009	358.15	12	2.417416667
Cold Stream 4		358.15		
Total Heat	27.782	371.15	13	2.137076923
Cold stream 5		213.05		
Total Heat	298.898	523.85	310.8	0.961705277
Cold stream6		523.85		
Total Heat	178.459	827.15	303.3	0.588391032
Hot stream1		348.35		
Total Heat	28.928	120.15	228.2	0.126765995
Hot stream2		371.15		
Total Heat	44.117	308.15	63	0.700269841
Hot stream3		289.85		
Total Heat	14.838	244.05	169.7	0.087436653
Hot Stream4		244.05		
Total Heat	19.851	120.15	123.9	0.160217918
Hot stream5		159.85		
Total Heat	6.231	135.15	24.7	0.252267206
Hot stream6		135.15		
Total Heat	25.73	38.15	97	0.265257732
Hot stream7		827.15		
Total Heat	283.938	120.15	707	0.401609618

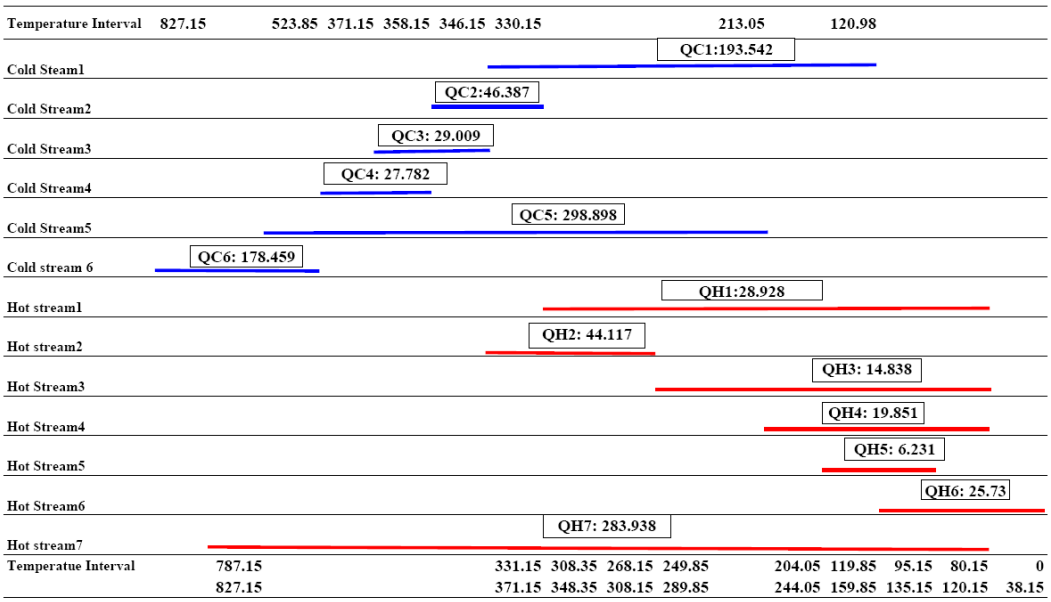
4.4.4 Minimum Approach Temperature

The Minimum Approach Temperature represents the smallest temperature difference at the sides of cold and hot streams entering and leaving exchangers. Smaller minimum temperature can achieve higher efficiency of heat exchange, while it also requires larger heat transfer areas, which need more capital investment. So, between the high heat transfer efficiency and capital investment, a trade-off has to be implemented. In the original design [65], the minimum approach temperature between cold and hot process streams was at the level of 40°C. To make a comparison at the same level, 40°C is chosen as the minimum approach temperature of the optimal heat exchanger network.

4.4.5 Heat Exchange Temperature Intervals

Upon the data in Table 4.1, a temperature interval table is built. As illustrated in Table 4.2, all the cold and hot streams are represented by horizontal lines.

Table 4.2: Heat Temperature Intervals



Temperature intervals are shown on the top and bottom rows. According to thermodynamic laws, heat transfer only occurs with the existence of a temperature difference. Since 40ºC is the minimum approach temperature of heat exchange, thus at the same temperature intervals the temperatures of hot streams must be 40 degrees higher than the temperature of cold streams. Both hot and cold streams are listed in the corresponding temperature range. Heat contents of each stream are also shown together with the lines. The table demonstrates all the matches between the hot and cold streams with the minimum 40°C approach temperature.

4.4.6 Heat Cascade Diagram

As shown in Figure 4.4, cold streams are shown on the left hand side, while hot streams are on the right.

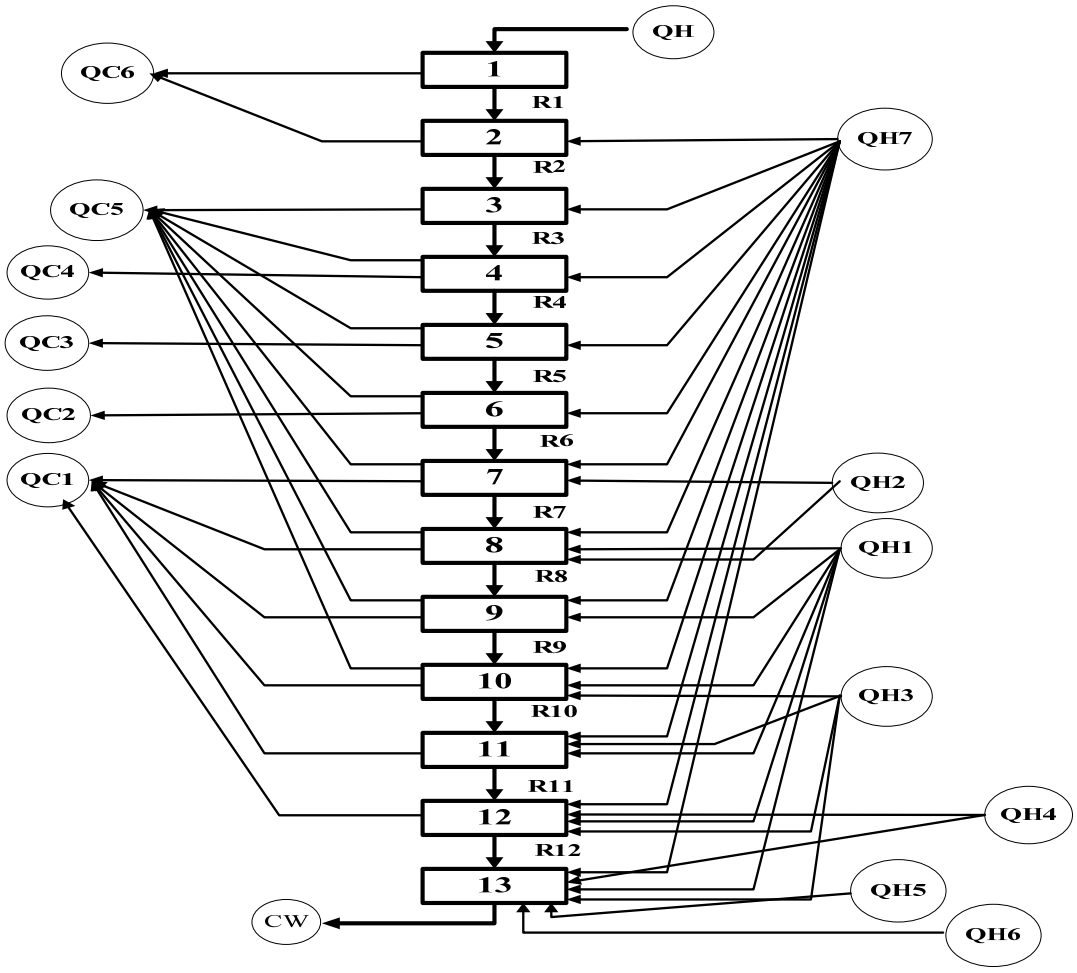


Figure 4.4: Heat Cascade Diagram

At each temperature interval, heat is transferred from the specific hot streams to the corresponding cold streams, and heat residual from the interval "cascades" down to the next interval. Heat can only be transferred when the hot streams are in the range of the temperature intervals. A cold stream can receive heat either from the hot streams at the same interval or an upper interval.

4.4.7 Transshipment Model of Heat Exchange [94]

As illustrated in Figure 4.5, hot utilities and hot streams supply heat to the cold streams, whereas cold utilities cool down the hot streams.

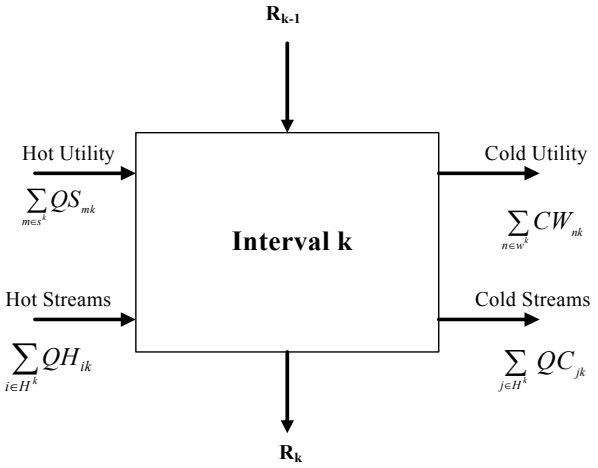


Figure 4.5: Heat Transfer at Interval 'k' [94]

There is also residual heat cascaded down from the upper temperature intervals. The purpose of heat integration is to minimize utility consumption from chemical processes. So, as a first step, objective function of the transshipment model is set to explore the minimum utility consumption. The objective function is defined as shown below:

Obj. Function:

$$Min.\sum_{k}\sum_{m\in S^k} QS_{mk} + \sum_{k}\sum_{n\in w^k} CW_{nk} \quad (4.1)$$

Constraints

$$R_{k-1} + \sum_{m\in S^k} QS_m + \sum_{i\in H_k} QH_{ik} = R_k + \sum_{n\in w^k} CW_{nk} + \sum_{j\in C^k} QC_{jk} \quad (4.2)$$

Where,

QS: Heat supply from hot utilities

CW: Heat extraction from cold utilities

QH: Heat supply from hot streams

QC: Heat extraction from cold streams

R_k: Heat residual from temperature interval k

The overall utility consumption is set as the objective function, and the energy balances between hot utilities, hot streams and cold utilities, and cold streams are set as constraints.

According to the transshipment model, the minimum utility consumption is achieved, and the "pinch" point is found at interval 12. However, the interactions between each cold stream and hot stream at every temperature interval are still unclear. The number of heat exchangers in the optimal solutions is also unknown. So, an expanded transshipment model is required to discover the heat transfer between each hot utilities, hot streams and cold utilities, cold streams.

4.4.8 Expanded Transshipment Model

As shown in Figure 4.6, the expanded transhipment model demonstrates the links between cold streams and hot streams.

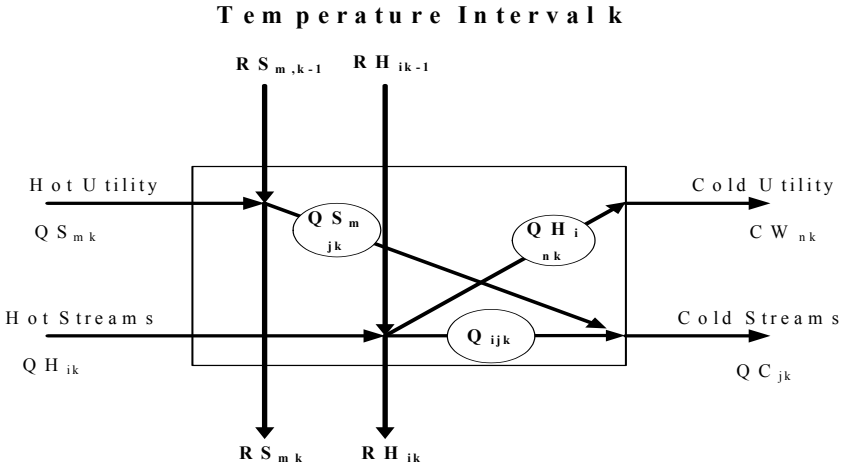


Figure 4.6: Detailed Temperature Interval [94]

Every hot stream is assumed to supply the heat to the cold stream and cold utility. Heat residual flows down to the next interval. In a similar way, hot utility is also assumed to transfer heat to each cold stream and leave heat residual, but considering the minimum utility consumption, there is no heat transfer from hot utility to cold utility

Thus the expanded transshipment model is written as:

Objective Function

$$\textbf{Min}.\ \sum_{k}\sum_{m\in S^{k}} QS_{mk} + \sum_{k}\sum_{n\in w^{k}} CW_{nk} \tag{19}$$

Constraints

$$RH_{i,k-1} + QH_{i,k} = \sum_{j\in C^{k}} Q_{i,j,k} + \sum_{n\in w^{k}} Q_{i,n,k} + RH_{i,k} \tag{20}$$

$$RS_{m,k-1} + QS_{m,k} = \sum_{j\in C^{k}} QS_{m,j,k} + RS_{m,k} \tag{21}$$

$$\sum_{j\in C^{k}} Q_{i,j,k} + \sum_{j\in C^{k}} QS_{m,k} = QC_{j,k} \tag{22}$$

$$\sum_{n\in w^{k}} QH_{i,n,k} = CW_{n,k} \tag{23}$$

Where,

$QH_{i,k}$ is the heat content of hot stream i at temperature interval k.

$Q_{i,j,k}$ is the heat transferred from hot stream i to cold stream j.

$Q_{i,n,k}$ is the heat transferred from hot stream to cold utility n.

$QS_{m,k}$ is the heat content of hot utility m at temperature k.

$QS_{m,j,k}$ is the heat transferred from hot utility stream m to cold stream j at interval k.

$RH_{i,k}$ is the heat residual of hot stream i from temperature interval k.

$RS_{i,k}$ is the heat residual of hot utility m from temperature interval k.

The optimal solution with minimum utility consumption and the links of hot and cold streams at each interval are achieved through the above model. Hot utility consumption was found to be 411.901 kW while cold utility consumption was 62.77 kW. Twenty-four heat exchangers were needed to build the optimal network, but this number is larger than the original design. Since it is

desirable not only to the minimum utility consumption but also to the number of heat exchangers, a new study is implemented with this objective in mind as discussed in the next section.

4.4.9 Expanded Transshipment Model with Logical Constraints

Binary variables are included in this model to represent the possibility of heat transfer between hot and cold streams. These binary variables stand for the number of heat exchangers. Prior to building the final model, the whole heat exchange network is first split into two sub-networks at the "pinch" point, and then in each sub-network the energy balances are set between each stream. This is based on the same approach as that of the previous model and results in a similar model. The objective function is changed to minimize the number of heat exchangers (Equ. 4.3), and logical constraints are added in this model (Equation 4.3, 4.4, 4.5, and 4.6). Hot and cold utilities consumptions at each temperature intervals are predetermined as constants with the same value as optimal results achieved in Section 4.7.

Objective function:

$$\text{Min.} \quad \sum_i \sum_j Y_{i,j} + \sum_i \sum_n Y_{i,n} + \sum_m \sum_j YS_{m,j} \tag{4.3}$$

Where,

$$Y_{i,j} = \begin{cases} 1, & \text{heat transferred from hot stream i to cold stream j} \\ 0, & \text{no heat transferred from hot stream i to cold stream j} \end{cases}$$

$$Y_{i,n} = \begin{cases} 1, & \text{heat transferred from hot stream i to cold utility n} \\ 0, & \text{no heat transferred from hot stream i to cold stream n} \end{cases}$$

$$YS_{m,j} = \begin{cases} 1, & \text{heat transferred from hot utility n to cold stream j} \\ 0, & \text{no heat transferred from hot utility n to cold stream j} \end{cases}$$

Logical Constraints:

$$\sum_k Q_{i,j,k} - U_{i,j} Y_{i,j} \le 0 \tag{4.4}$$

$$\sum_k Q_{i,n,k} - U_{i,n} Y_{i,n} \leq 0 \tag{4.5}$$

$$\sum_k QS_{m,j} - US_{m,j} Y_{m,j} \leq 0 \tag{4.6}$$

Where,

$U_{i,j}$ is the upper limit of heat transferred between cold stream j and hot stream j at interval k.

Similarly, $U_{i,n}$, $US_{m,j}$ are the upper limits of heat transferred from hot streams i to cold utility n and hot utility m to cold streams j respectively.

The purpose of logical constraints is to set the logic relations between binary variables and energy balances. So, when Y_{ij} is set to zero, the heat transfer between hot stream i and cold stream j will be automatically reset to the zero by the logical constraints.

The sequential models above, which were built in GAMS as shown in Appendix B, resulted in a 17-heat exchanger network. Hot and cold utilities energy consumptions were 413.214kW and 62.770kW respectively. Compared to the original design, the hot utility energy consumption was reduced by 8.6% while the cold utility energy was decreased by 38.18%.

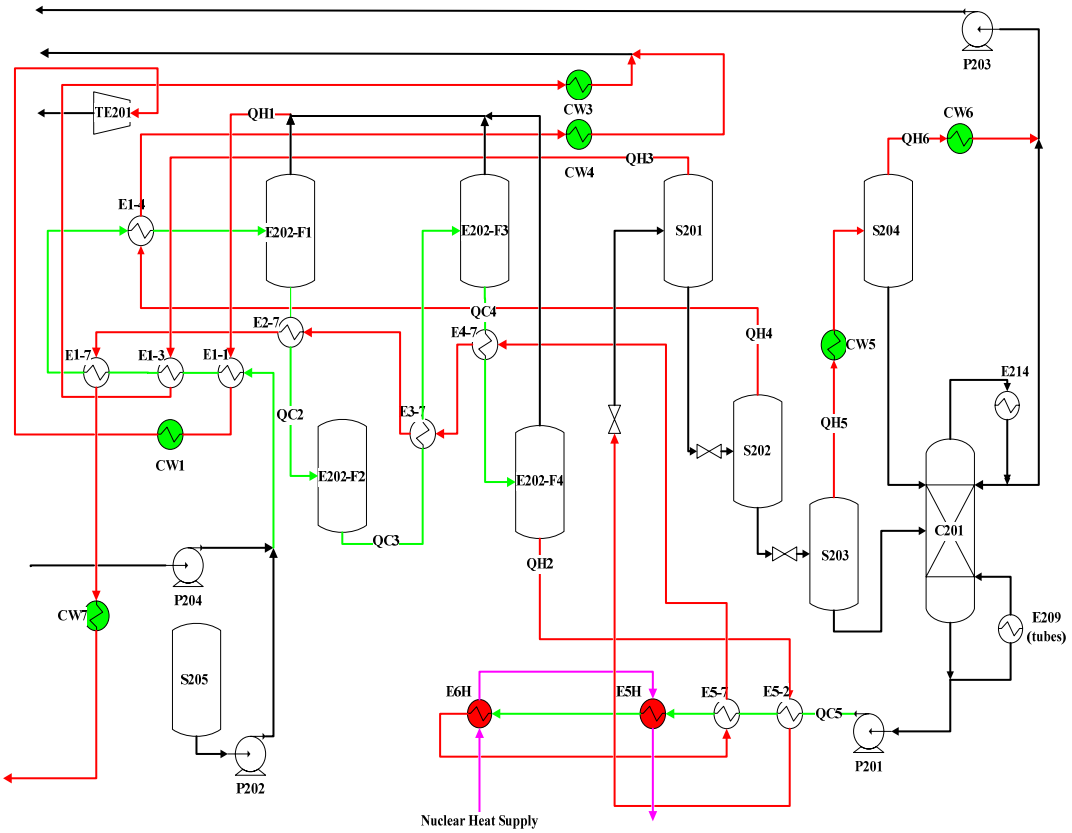


Figure 4.7: Optimized Heat Exchangers Network of H_2SO_4 Decomposition Process

4.5 Conclusions with Respect to Thermochemical Cycle

In this chapter, a brief survey of hydrogen production methods was conducted, and thermochemical hydrogen production via the S-I cycle was considered as a potential efficient method. Heat integration was implemented to improve process efficiency and decrease capital investment. A LP optimization model was first built to minimize utility energy consumption, and then an expanded transshipment model was defined to find the links between cold process streams and hot process streams, finally a mixed integer model was built to explore the minimum number of heat exchangers. As illustrated in Figure 4.7, based on the results achieved from previous models, an optimal network with 17 heat exchangers was established and 8.6% hot utility and 38.18% cold utility energy were saved.

Chapter 5 Conclusions and Recommendations

5.1 Conclusions

In the thesis, three scenarios were built to project the market development of hydrogen fuel cell vehicles in Ontario. Upon projected hydrogen demand from all fuel cell vehicles in Ontario, cost of hydrogen was investigated. The thermochemical S-I cycle was also studied and a linear integer mixed model was established to implement the heat integration of S-I cycle. The conclusions were drawn, shown as follows,

- As a mature technology, water electrolysis is considered as a good option to generate hydrogen. Distributed water electrolysis generation facilities can be built to meet hydrogen demand during the transition period to a hydrogen economy, whereas large scale centralized water electrolysis production plants will be required when hydrogen fuel cell vehicles market are highly developed.
- In order to meet hydrogen demand from all fuel cell vehicles in Ontario, as shown by the models, an additional power supply, over one-third of the current Ontario's installed power generation capacity will be needed for water electrolysis production in 2050, and at this time for scenario 1, 2 and 3, there will be to totally 8.35, 9.40 and 10.2 millions FCVs respectively in Ontario.
- Assuming current central Canada hydrogen production surplus, 22.154 million kg/year are all supplied to FCVs in Ontario, and the hydrogen surplus can meet the demand from FCVs in Ontario until 2023 for scenario 1, 2 and 2018 for scenario 3.
- During the transition period to a hydrogen economy, distributed electrolyzers can be first built to meet hydrogen demand from small fleets of FCVs in Ontario. Assuming Hydrogenics IMET-1000 (60 Nm^3H_2/hr) as a standard model, about 293, 342 and 750

electrolyzer units will be needed for scenario 1, 2 and 3 respectively, and these units can meet hydrogen demand from FCVs in Ontario until 2025 for scenario 1, 2 and 2020 for scenario 3. After that year, as FCVs market expands and hydrogen demand increases, costs of hydrogen starts to level off, and this is the time that centralized electrolyzers would be mostly needed.

- In both of hydrogen production and distribution pathways studied in Chapter 3, from 2016 to 2050, cost of hydrogen from the production site in Bruce region to the consumers in the GTA ranges from 8.40-3.18$/kg for gaseous hydrogen and 8.05-3.66$/kg for liquid hydrogen.
- Cost of hydrogen generated by water electrolysis is highly sensitive to electricity price. A small increment of electricity price can cause considerable increase of hydrogen cost. Cost of hydrogen is insensitive to water price at the current price of water. However, impact of water price may become noticeable when the water price starts to increase because of vast water consumption from hydrogen production.
- With respect to cost of hydrogen delivery, pipeline distribution may be preferable for large scale hydrogen production whilst cryogenic truck transportation is recommendable for small scale production.
- Hydrogen thermochemical cycles are always considered to an important alternative to other convention methods. As thermochemical cycles only consume heat, thermochemical cycles generally have a greater projected efficiency and can be improved effectively through heat integration, which can be implemented by optimization methods.

5.2 Recommendations

The followings are the recommendations for the future research:

- High temperature steam electrolysis is not investigated in the thesis as high temperature electrolysis technology is currently not fully applicable and there is not sufficient data available to support the detailed study. However as an alternative hydrogen generation method, high temperature electrolysis is expected to be more efficient than conventional water electrolysis. So it is still worthy of a future detailed study when the technology can advance beyond the early stage of research.
- Thermochemical cycles have the potential to be the most efficient hydrogen production method and are suitable for centralized large scale production. Studies of thermochemical cycles are a very important supplement for hydrogen production pathway analysis. In the future study, more cycles such as UT-3 cycle and Cu-Cl should also be involved in the detailed investigation. The Studies should also include integration o heat usage in order to improve system efficiency.
- For the study of hydrogen distribution, ship and rail delivery are not investigated in the thesis, but they are still the very important transportation approaches. For the cities with ports or rails, these two methods are more efficient and economic than other conventional measures.

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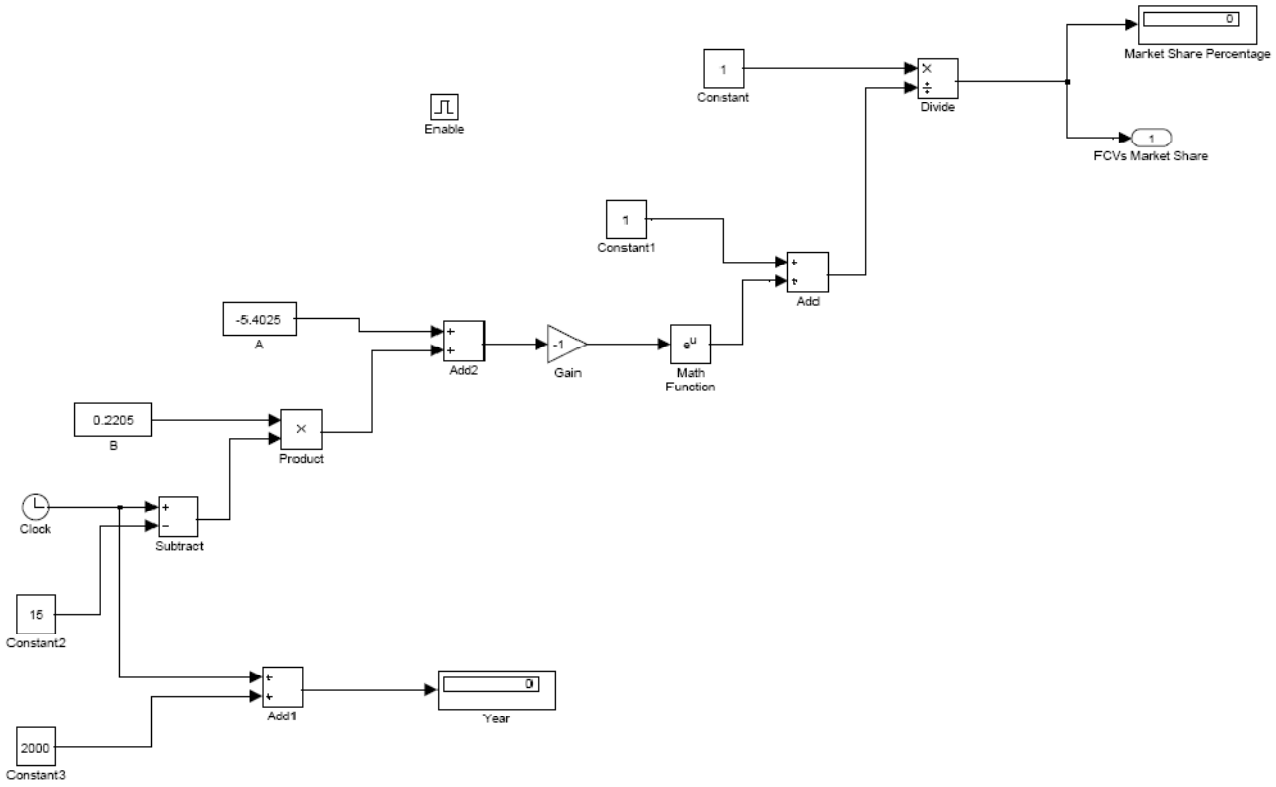
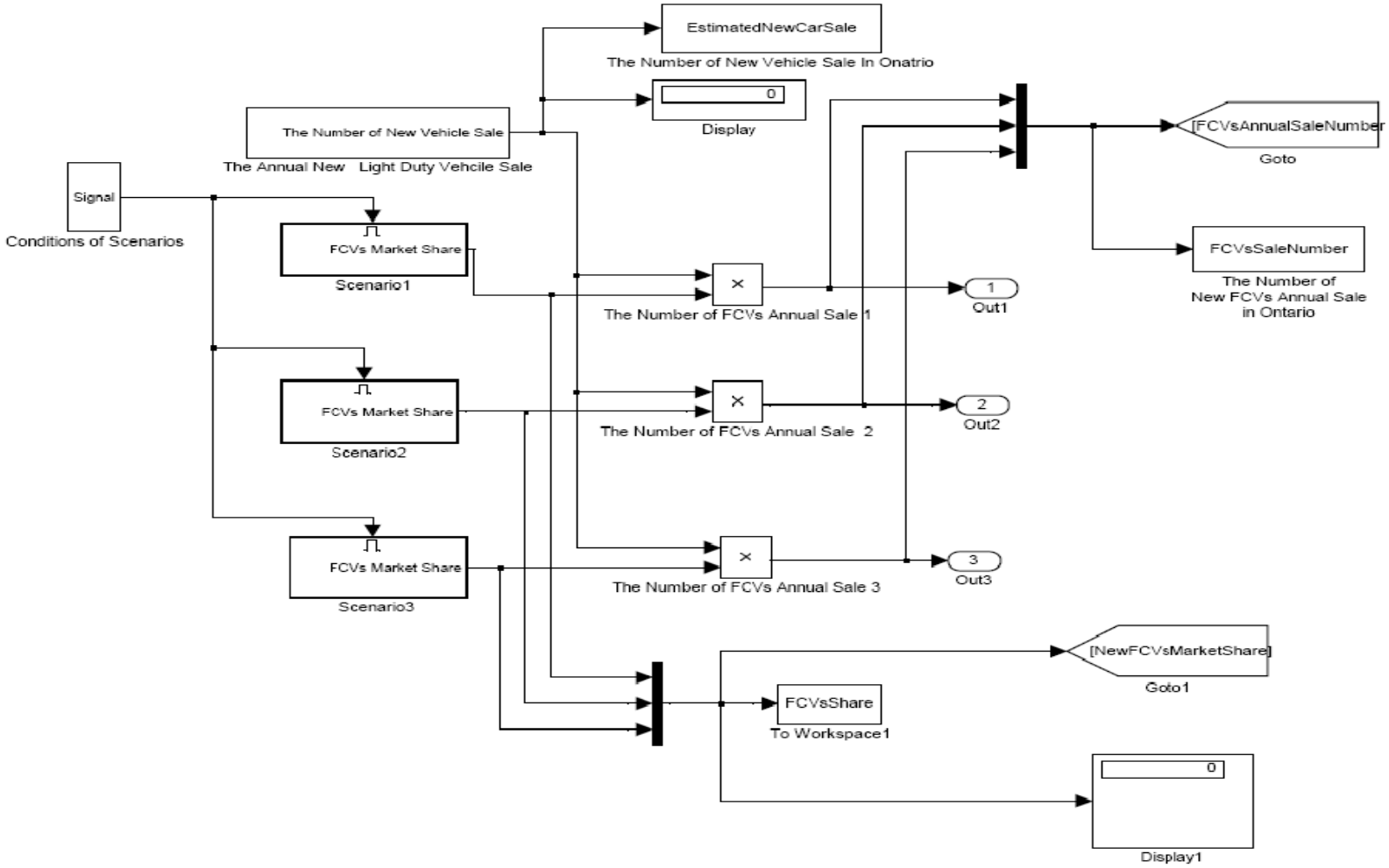
Appendix A

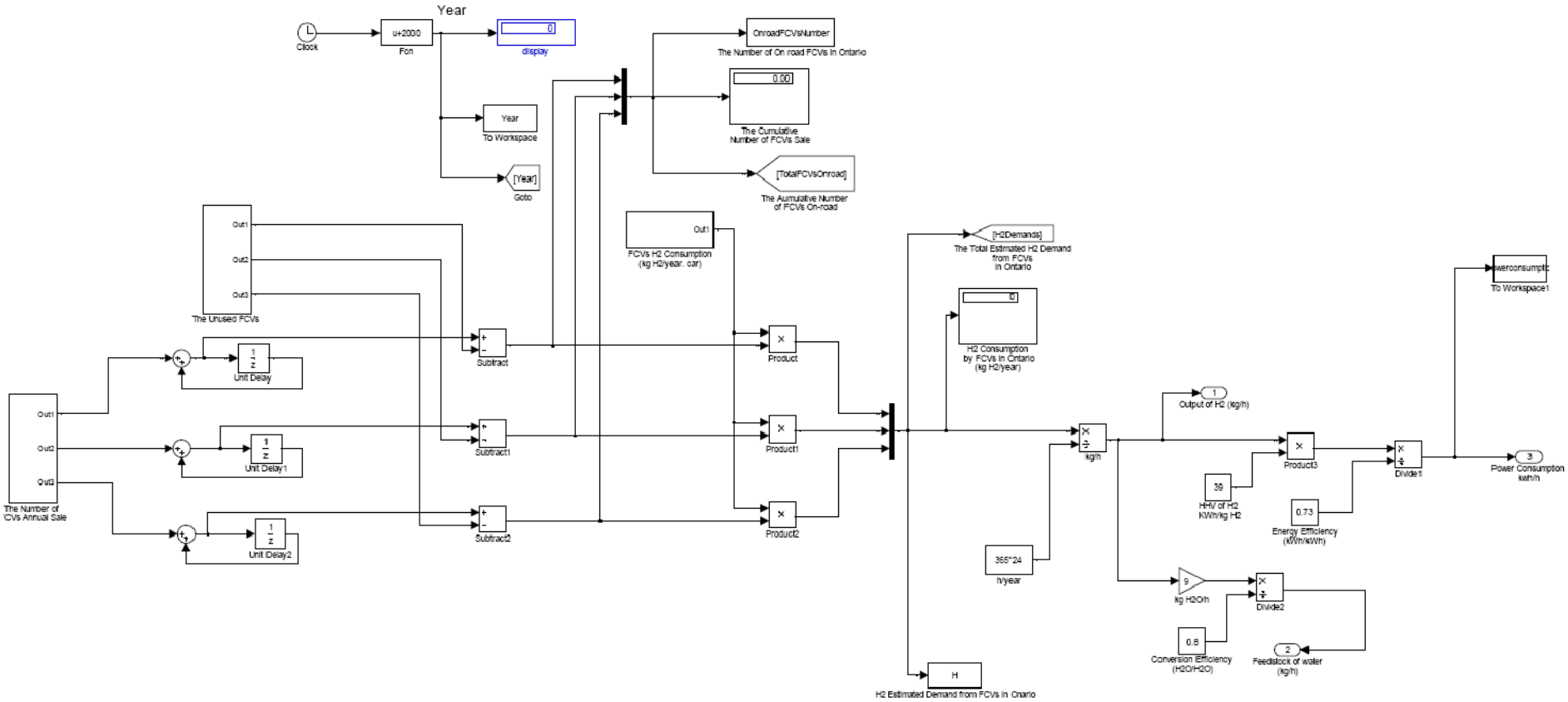
Flowsheets of Hydrogen Demand and Production Analysis Simulink Model



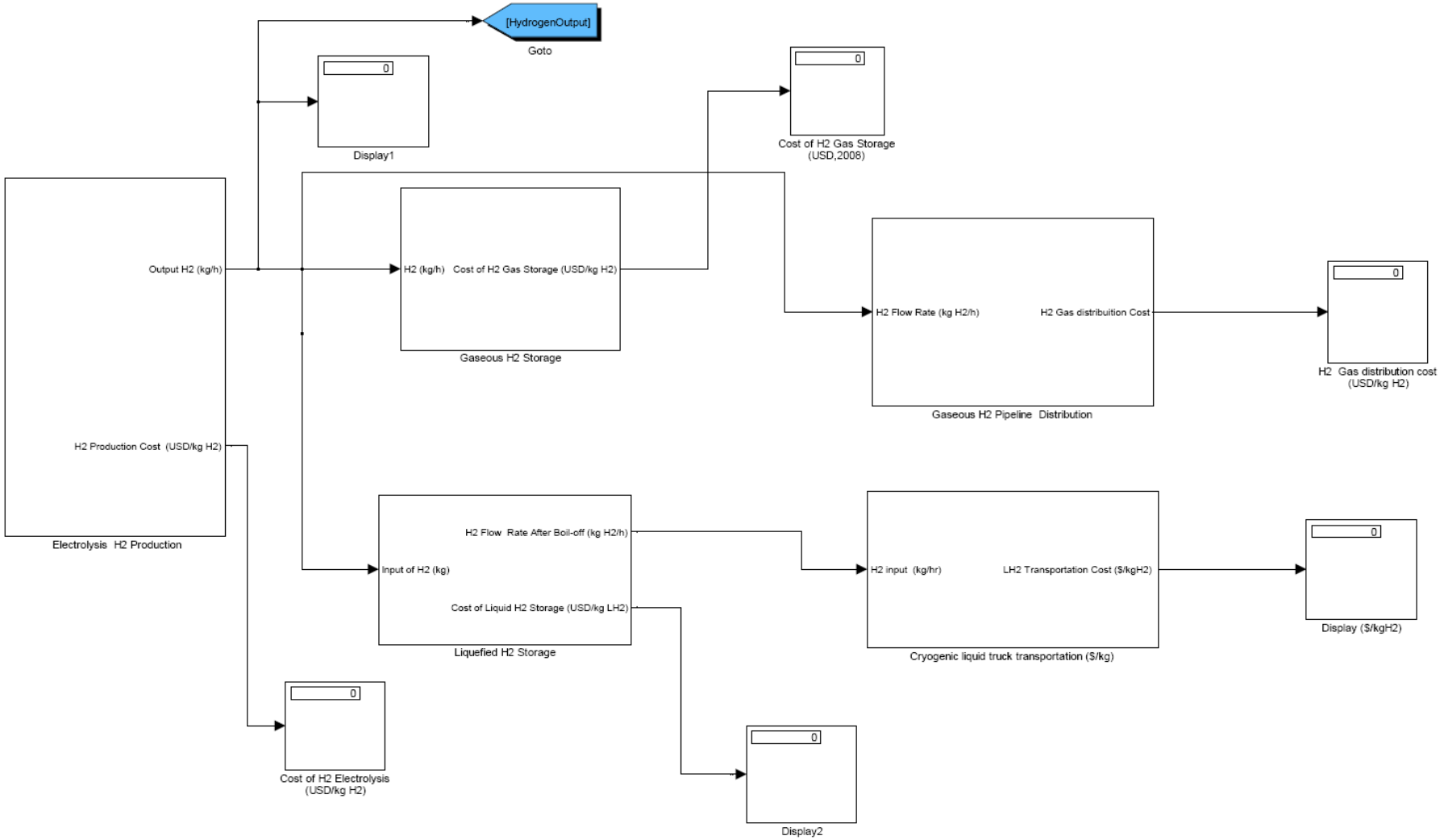
A1: Ontario's H_2 FCVs Market Share Estimation Model



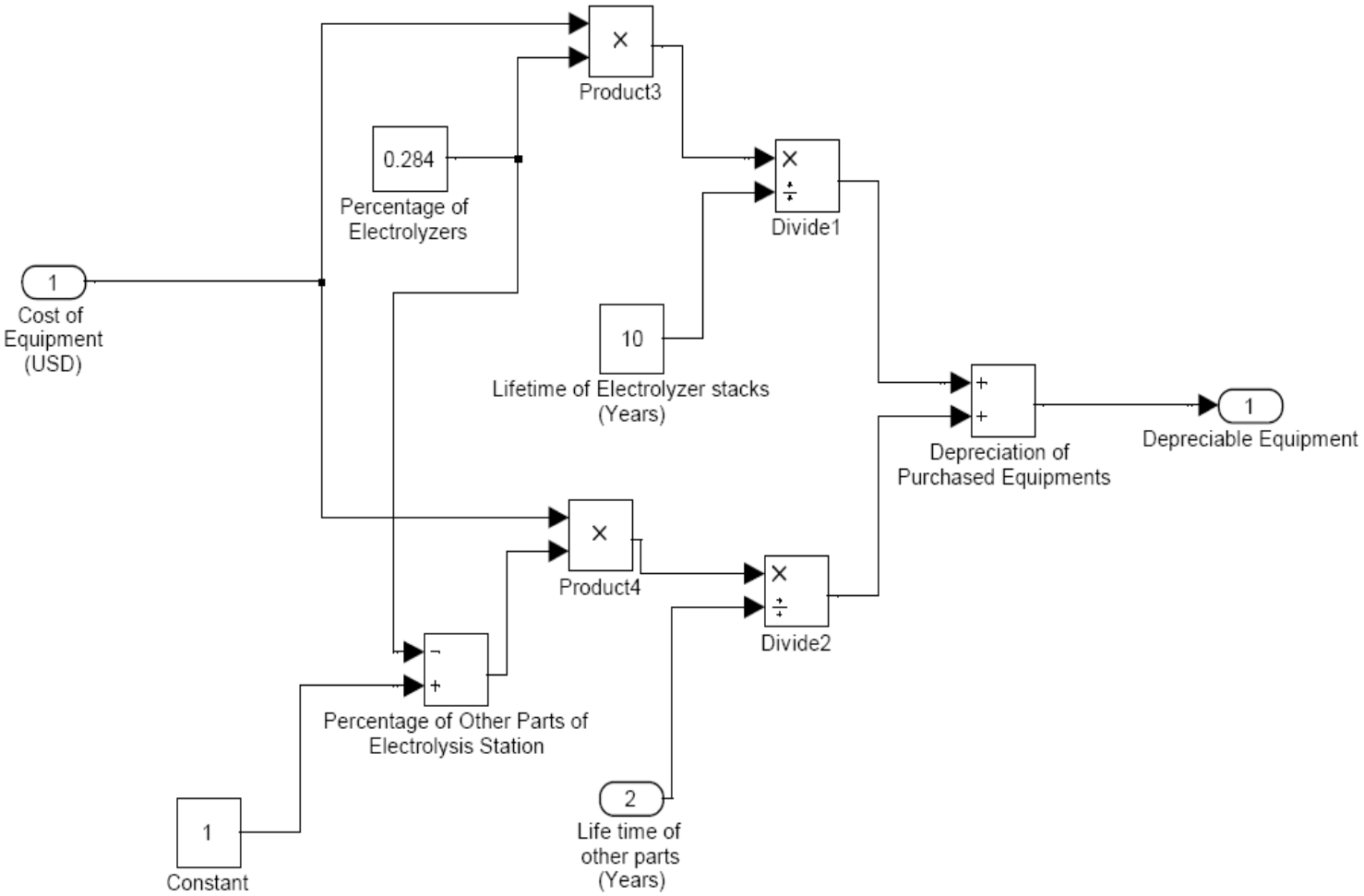
A2: The Number of Ontario's New H_2 FCVs Estimation Model



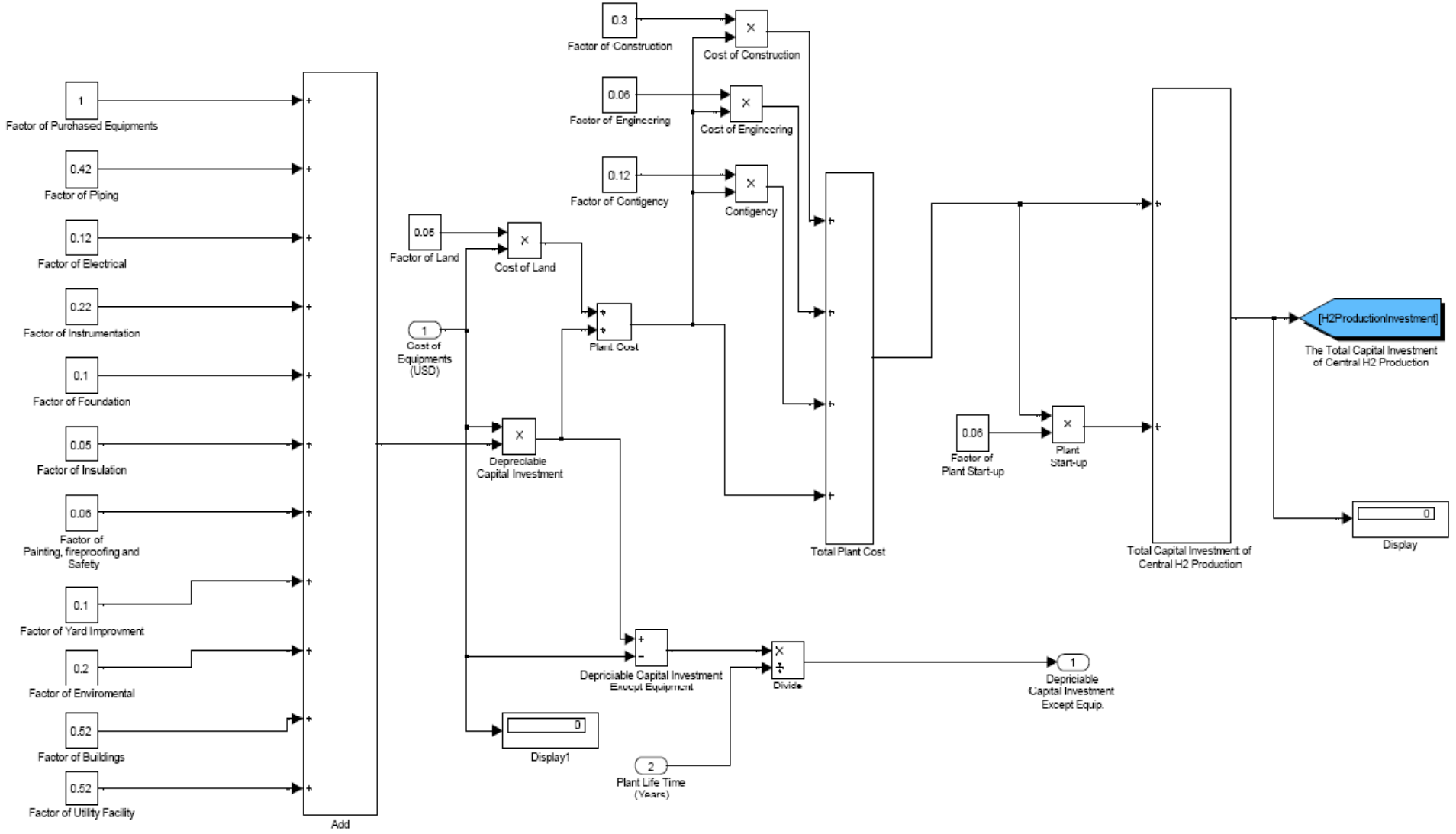
A3: The total number of Ontario's on-road H_2 FCVs Estimation Model



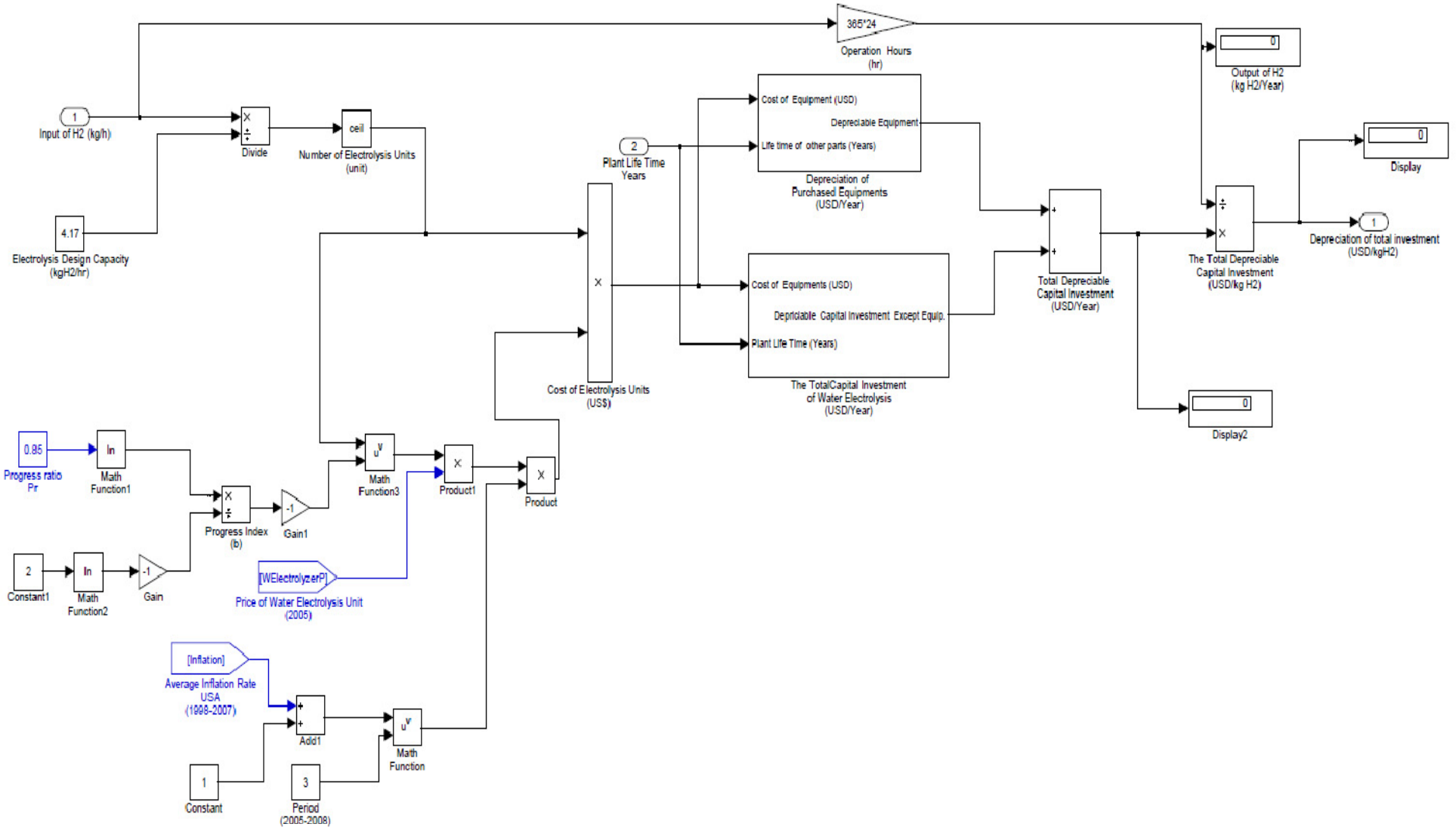
A4: Hydrogen Demand and Production Estimation Model



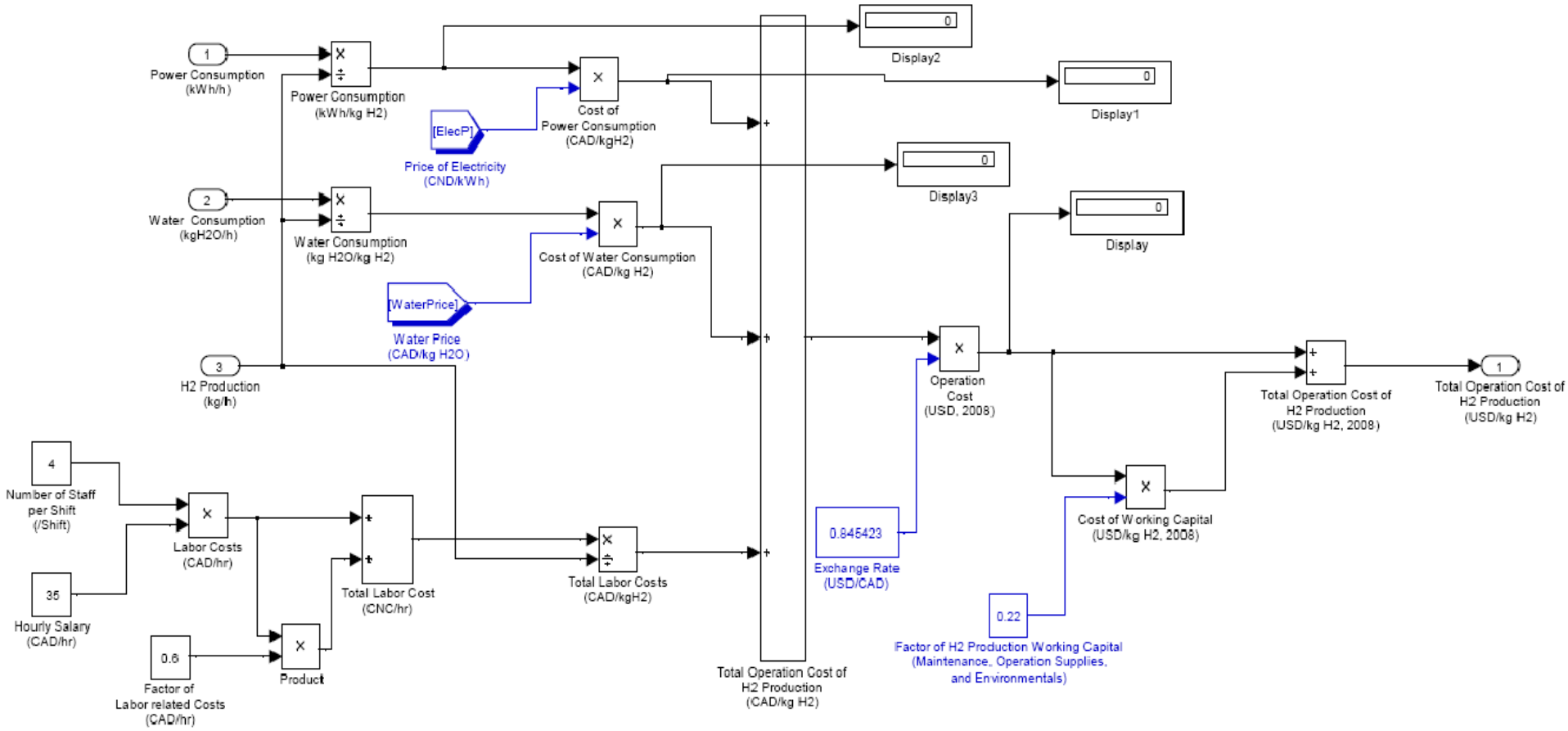
A5: Cost of Electrolyzers Estimation Model



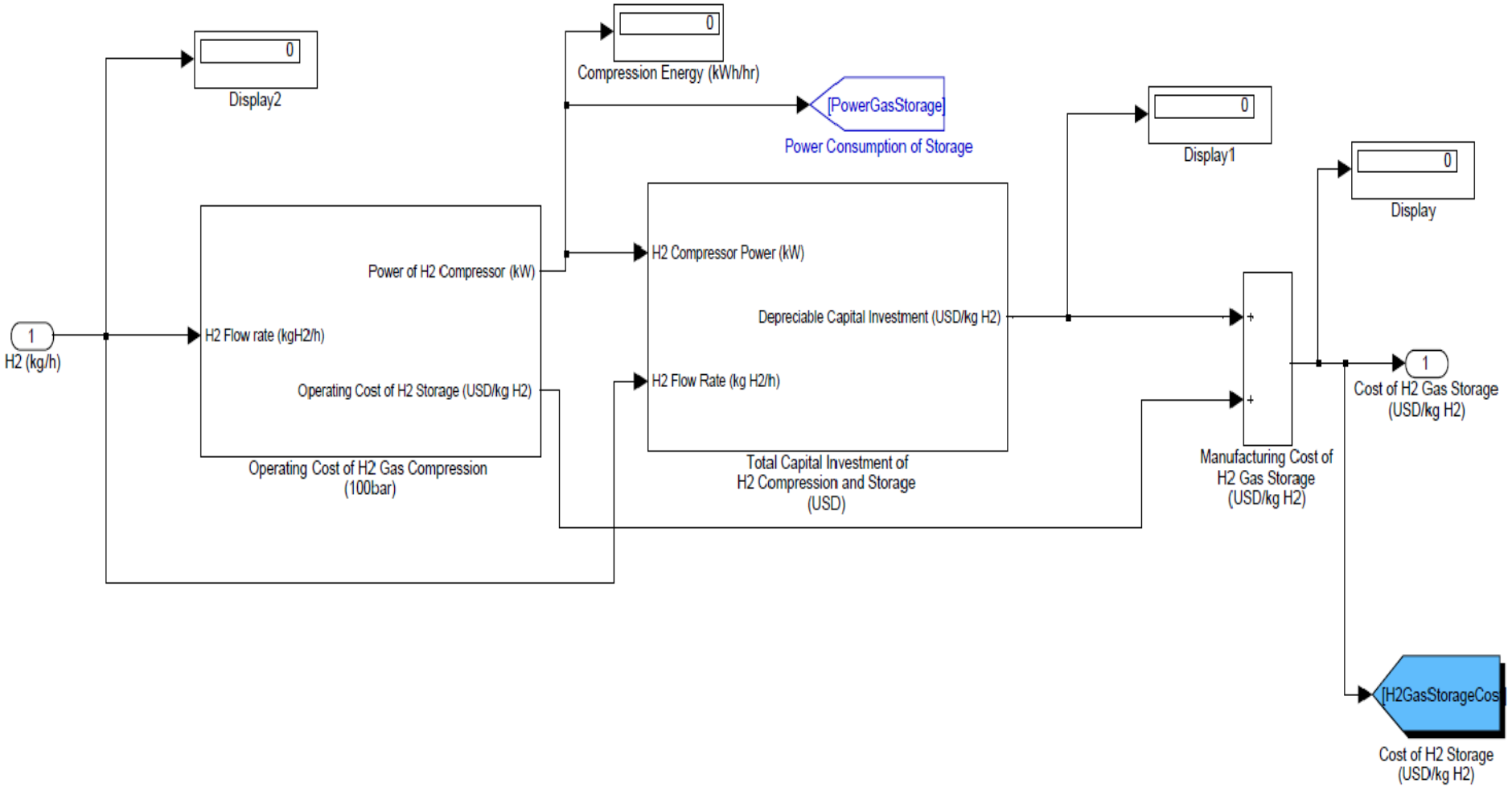
A6: Electrolysis Capital Investment Estimation Model



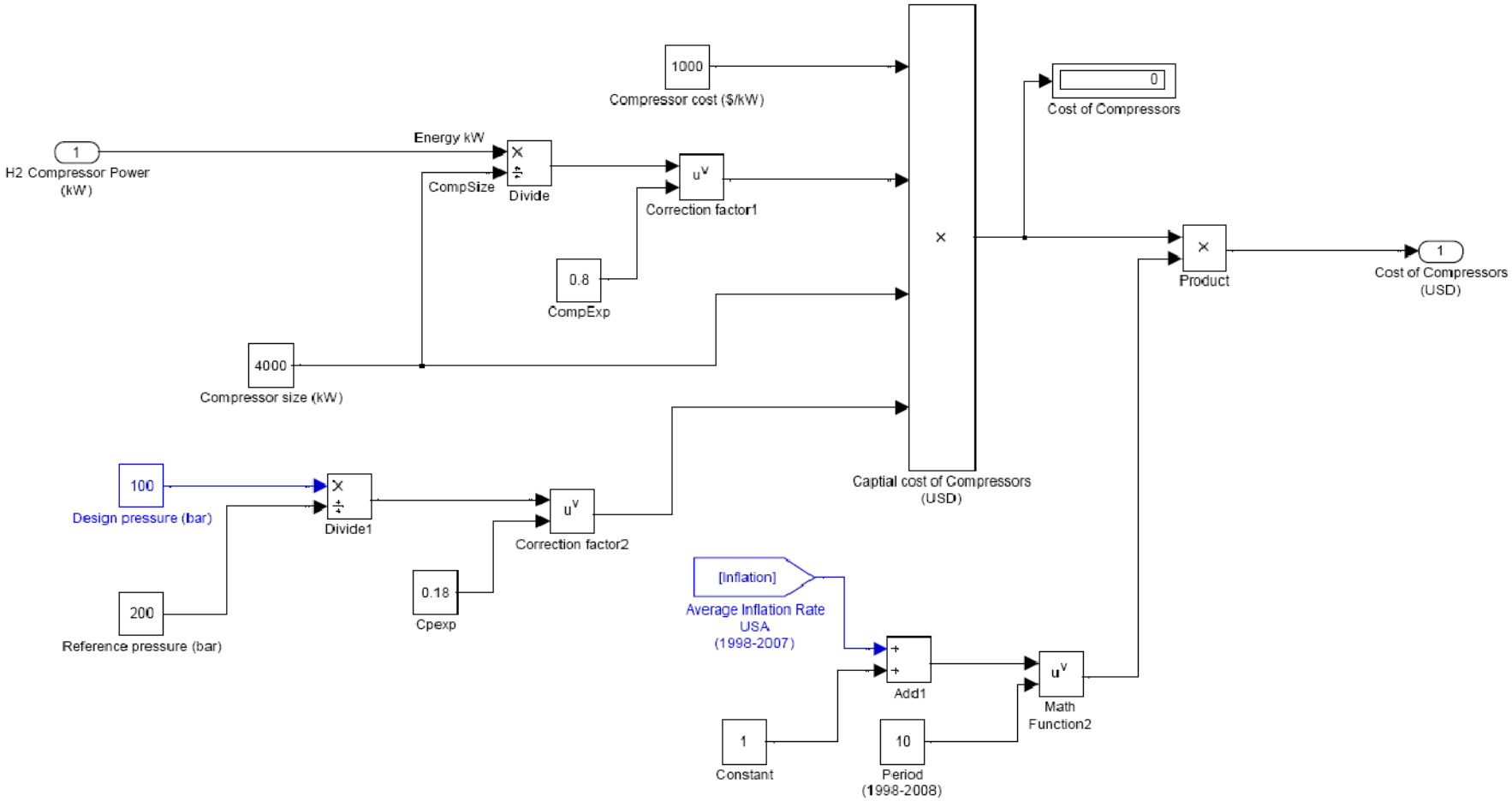
A7: Depreciation of Electrolysis Capital Investment Estimation Model



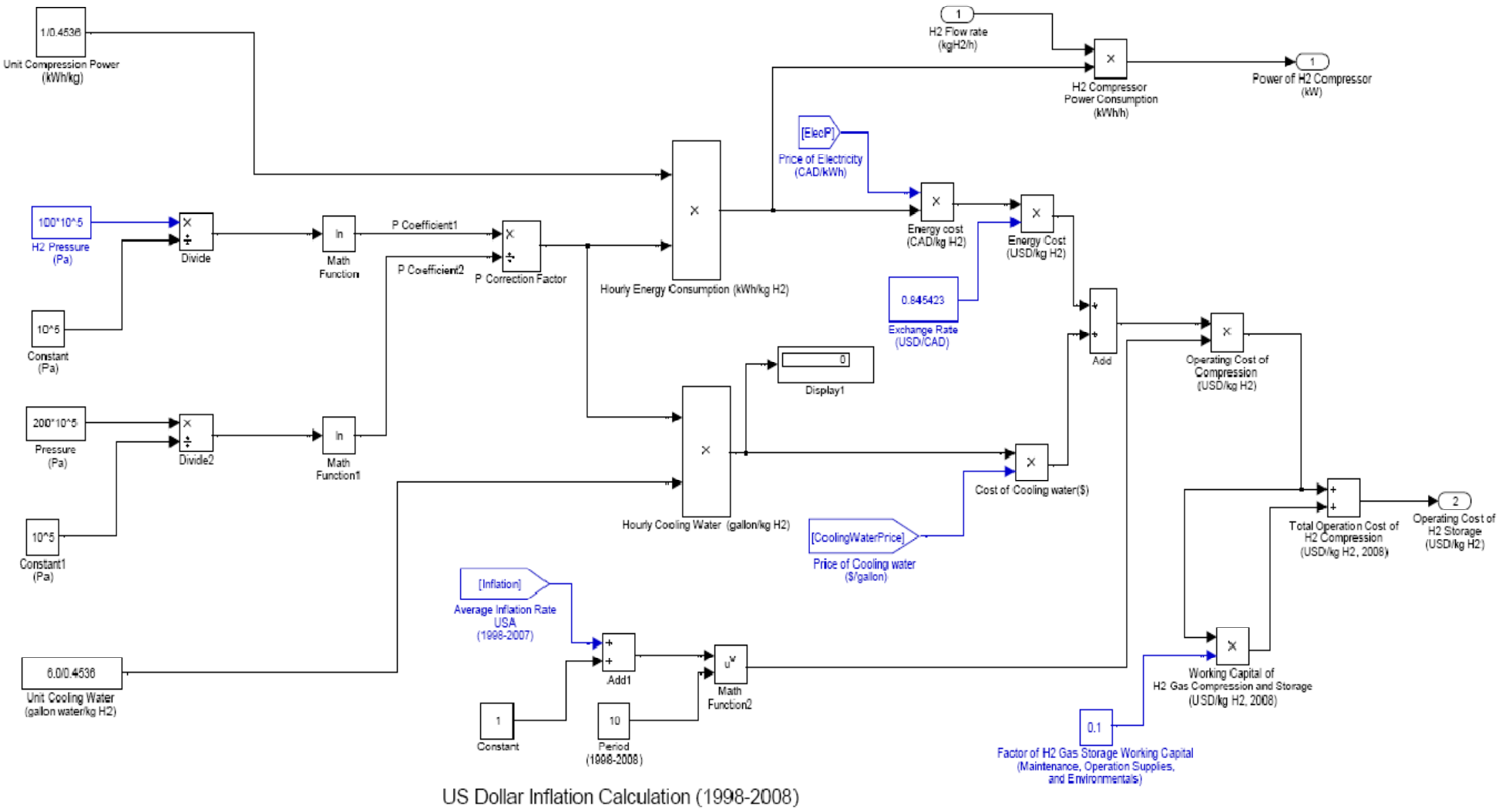
A8: Operating Cost of Electrolysis Estimation Model



A9: Total Cost of Gaseous Hydrogen Storage Estimation Model

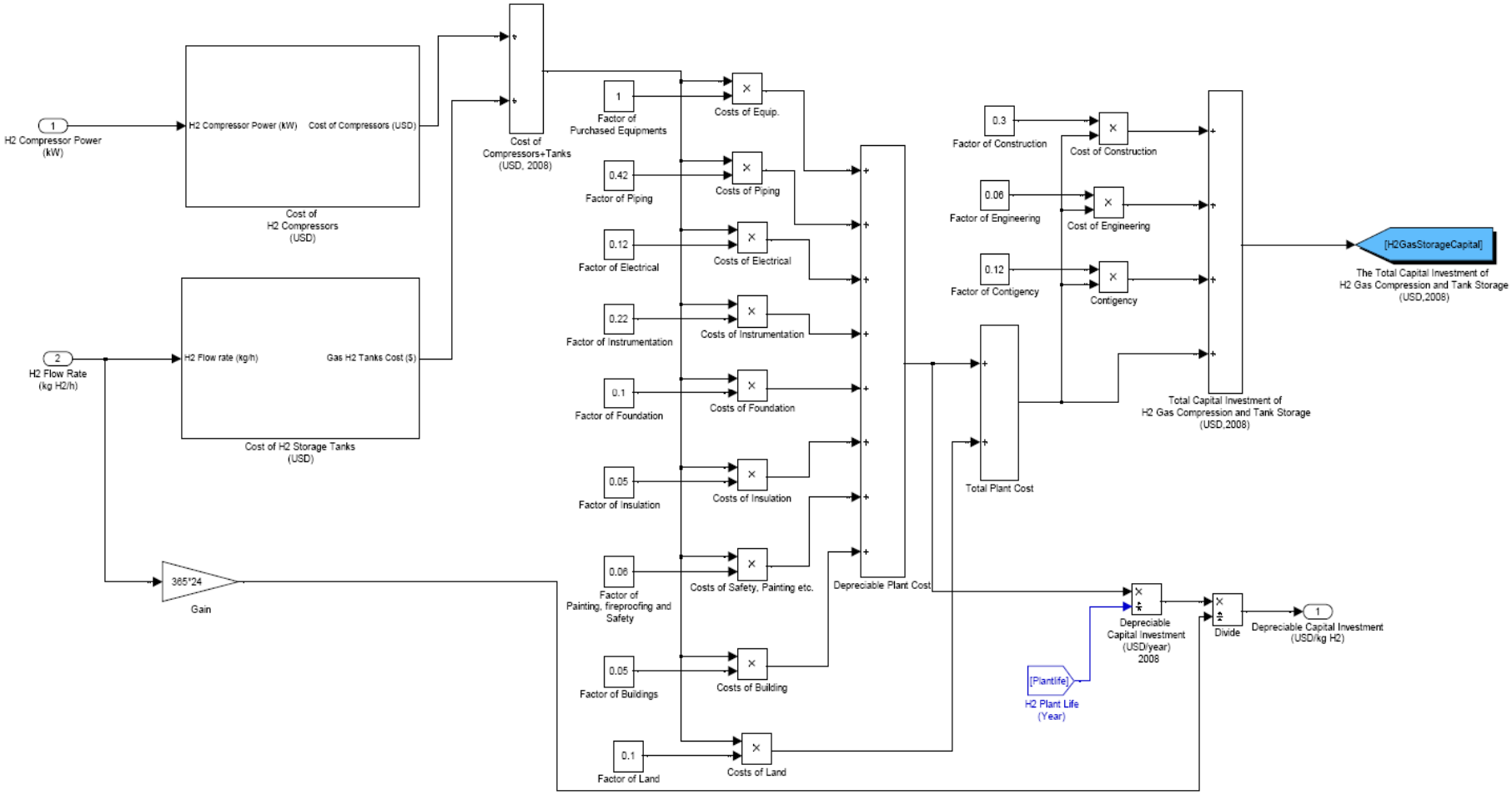


A10: Cost of Hydrogen Compressors Estimation Model

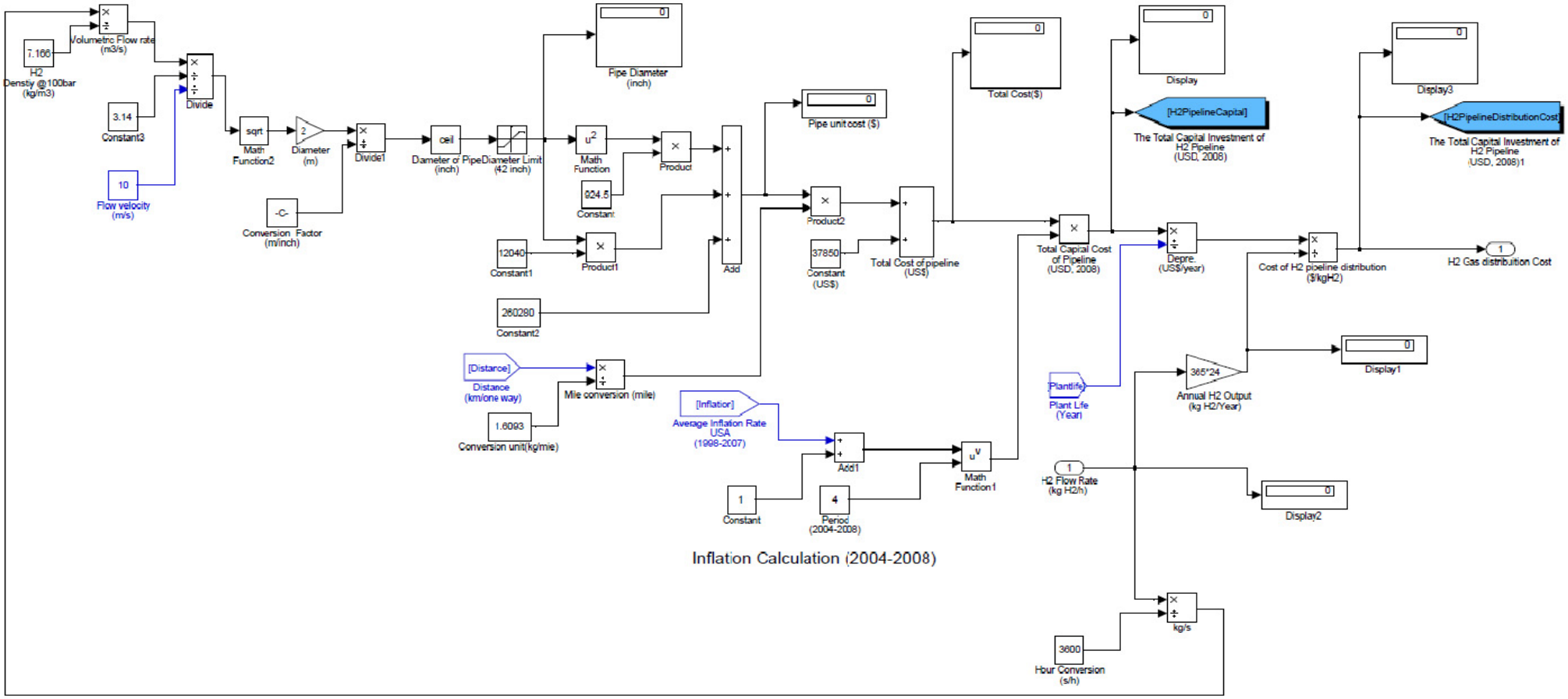


US Dollar Inflation Calculation (1998-2008)

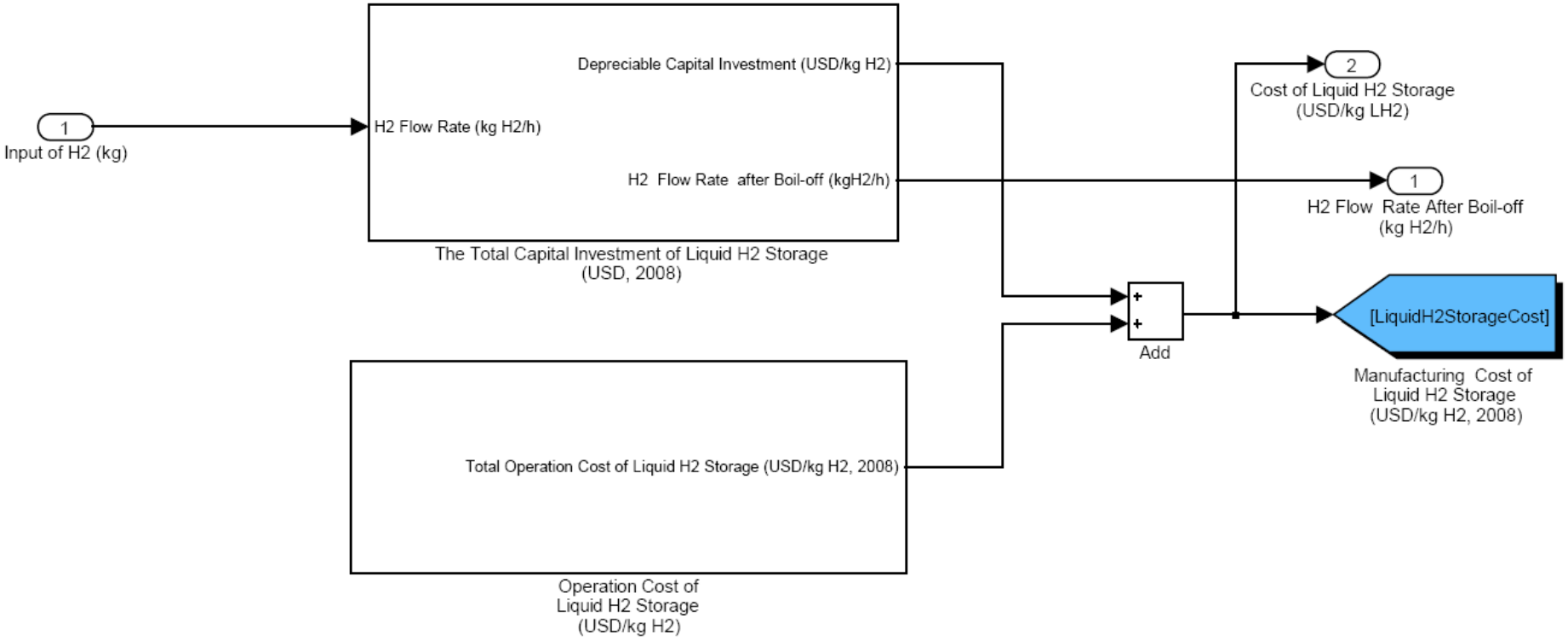
A11: Operating Cost of Gaseous Hydrogen Storage Estimation Model



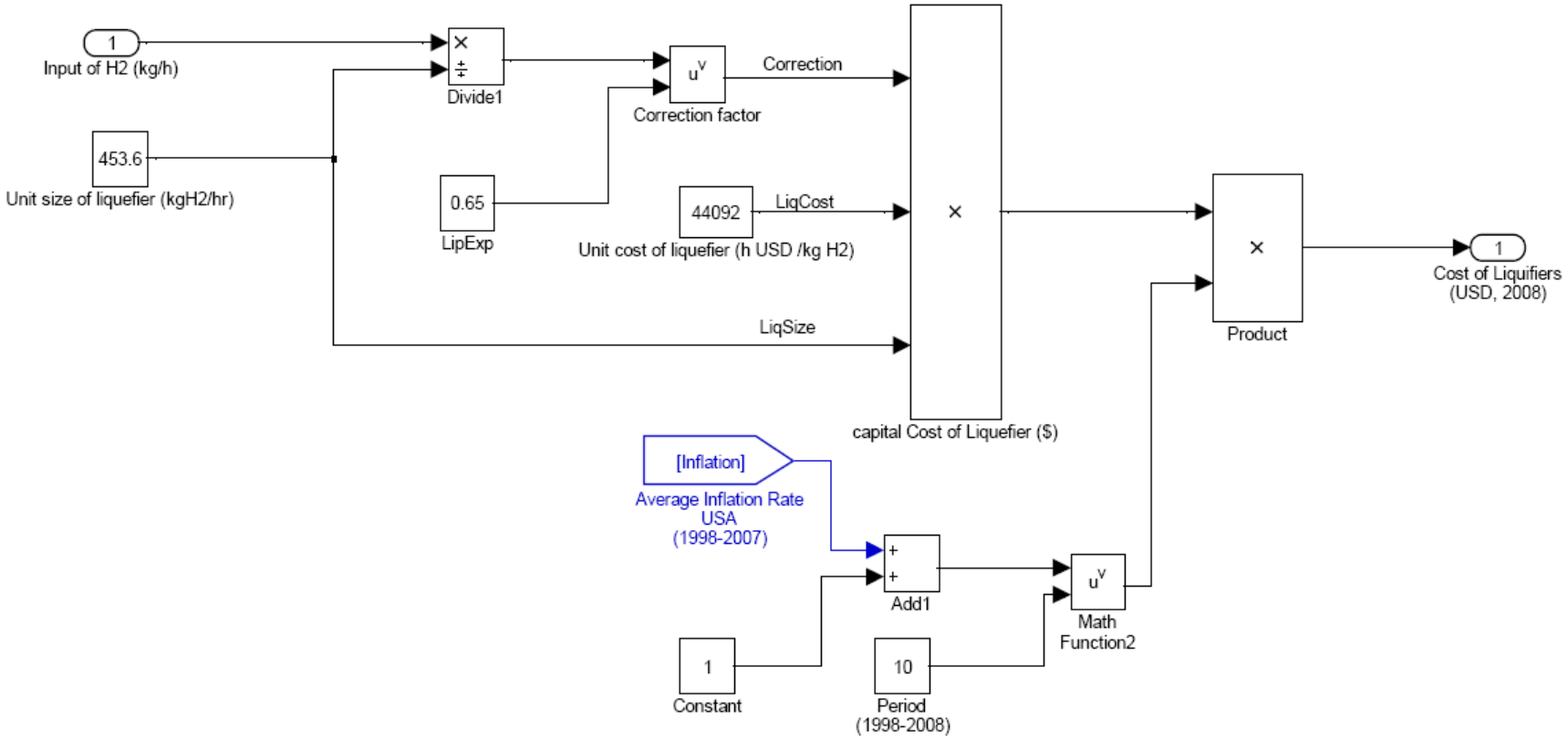
A12: Capital Investment of Gaseous Hydrogen Storage Estimation Model



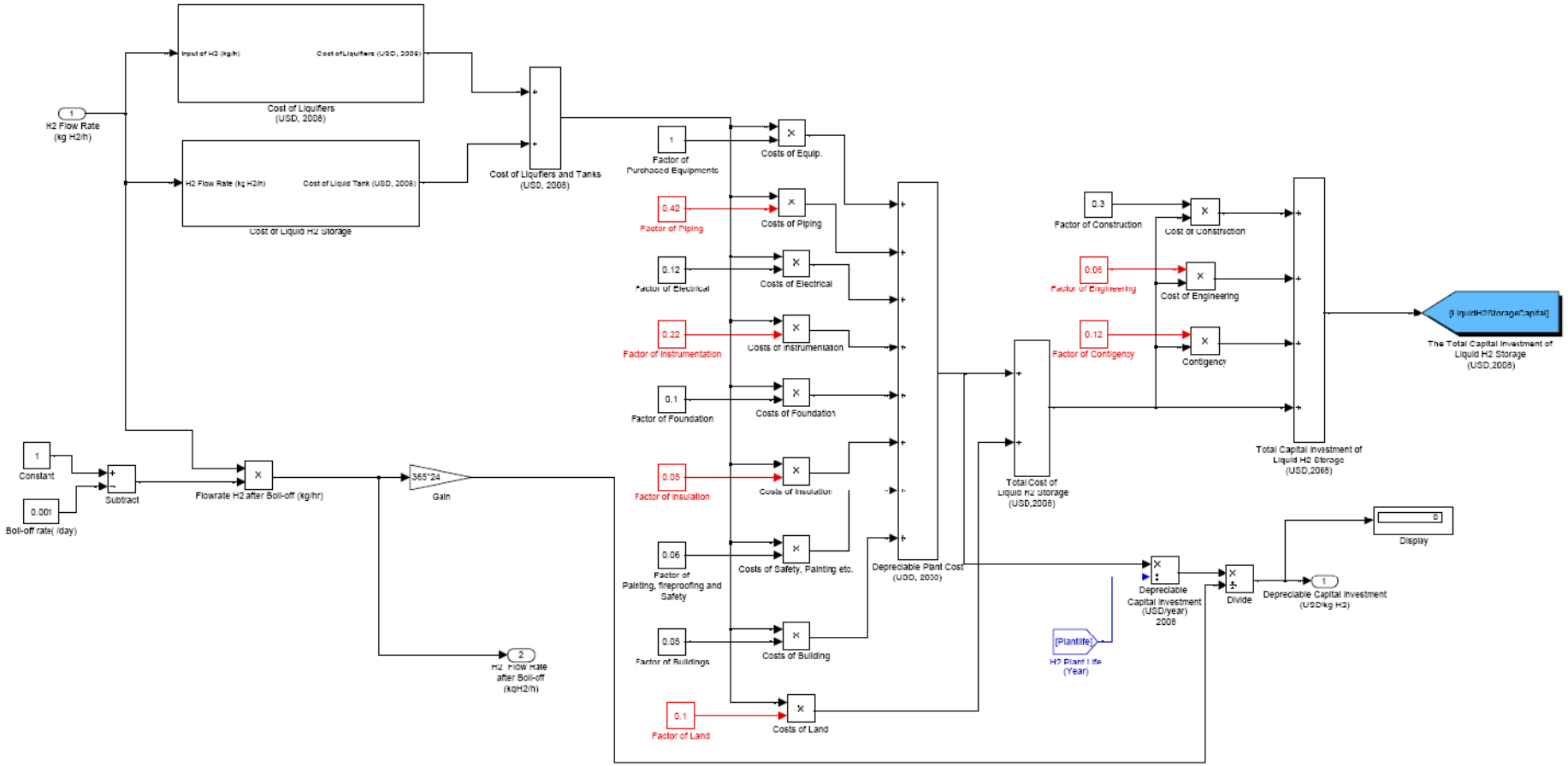
A13: Total Cost of Hydrogen Pipeline Distribution Estimation Model



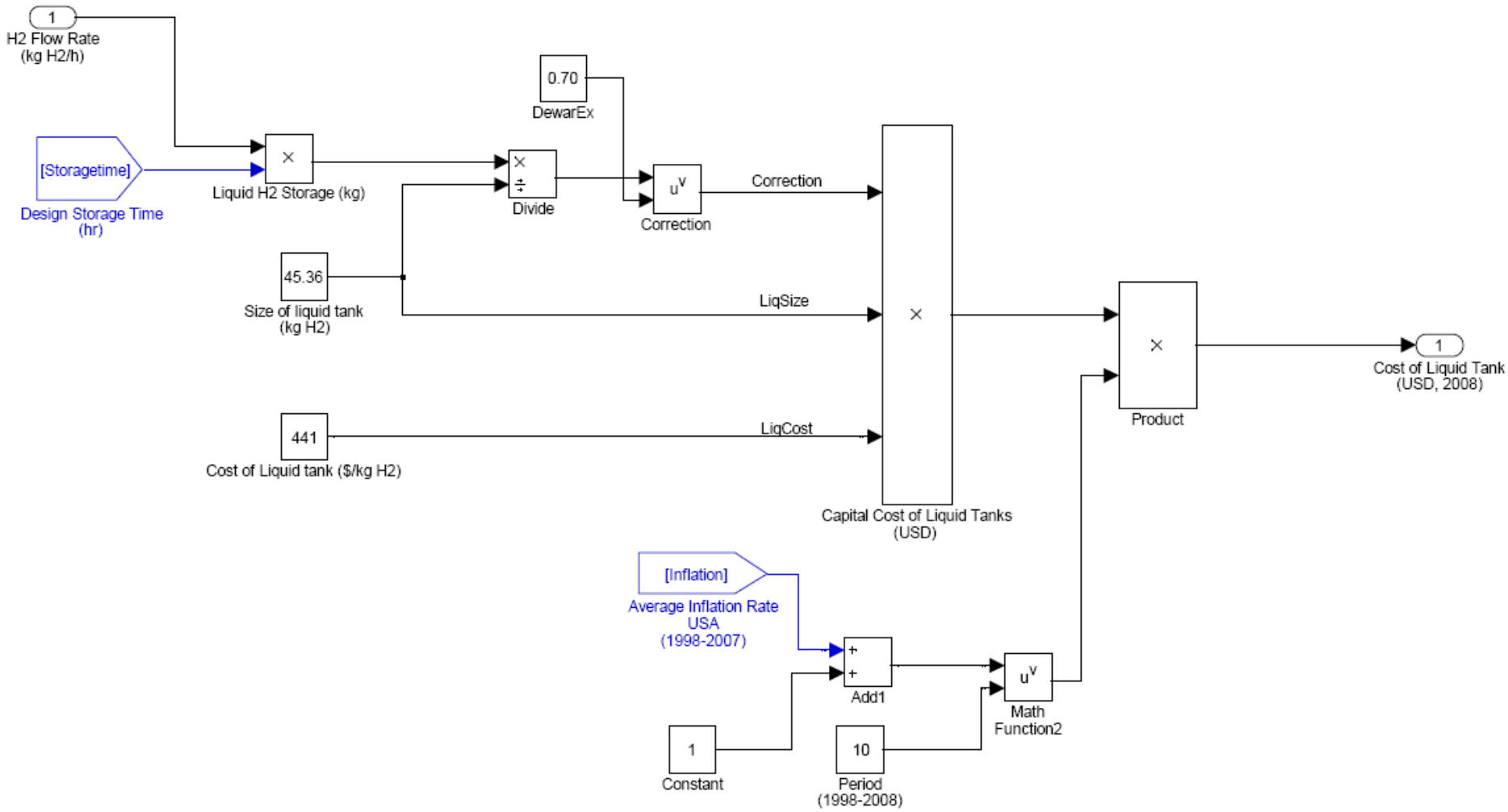
A14: Total Cost of Liquid Hydrogen Storage Estimation Model



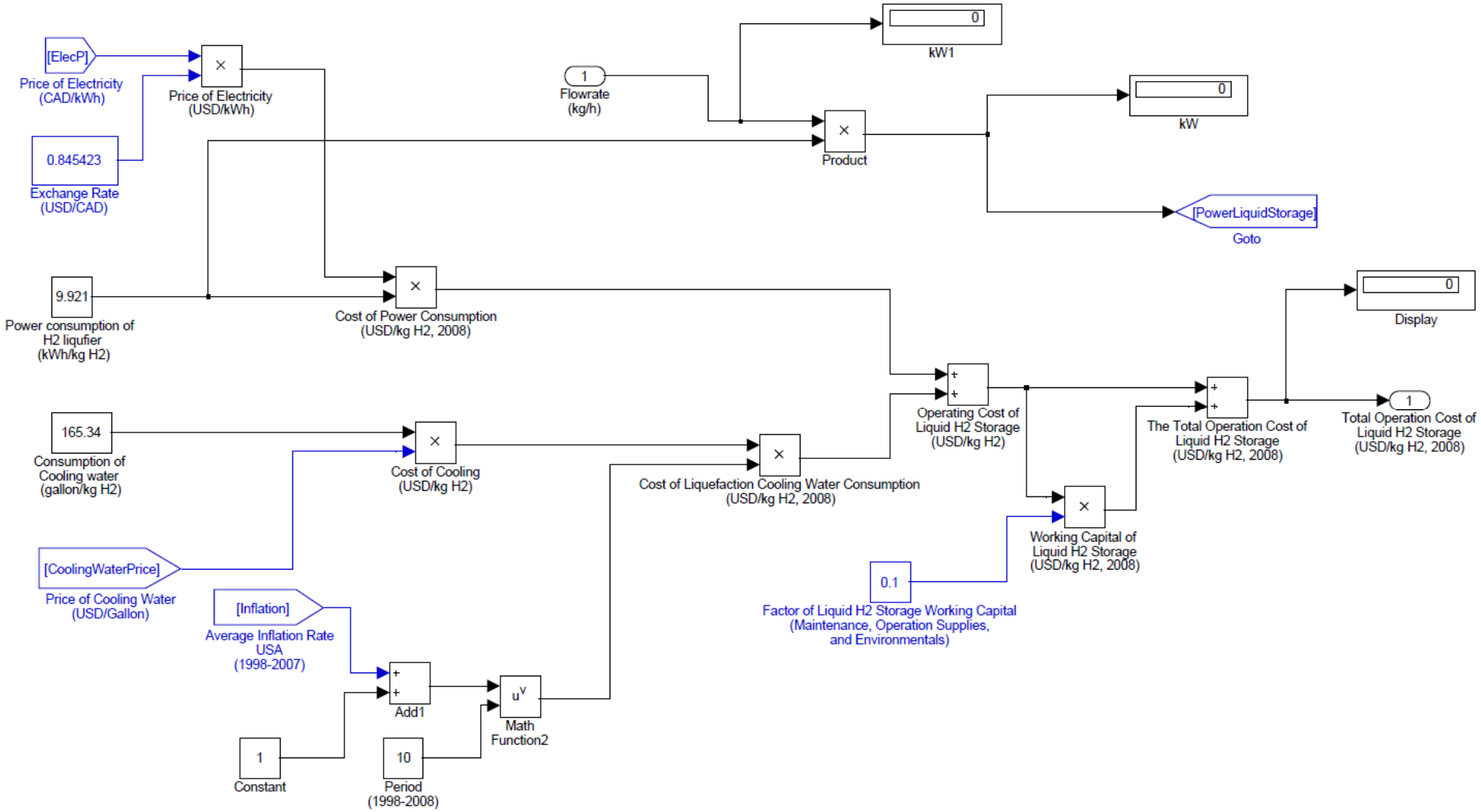
A15: Cost of Hydrogen Liquefiers Estimation Model



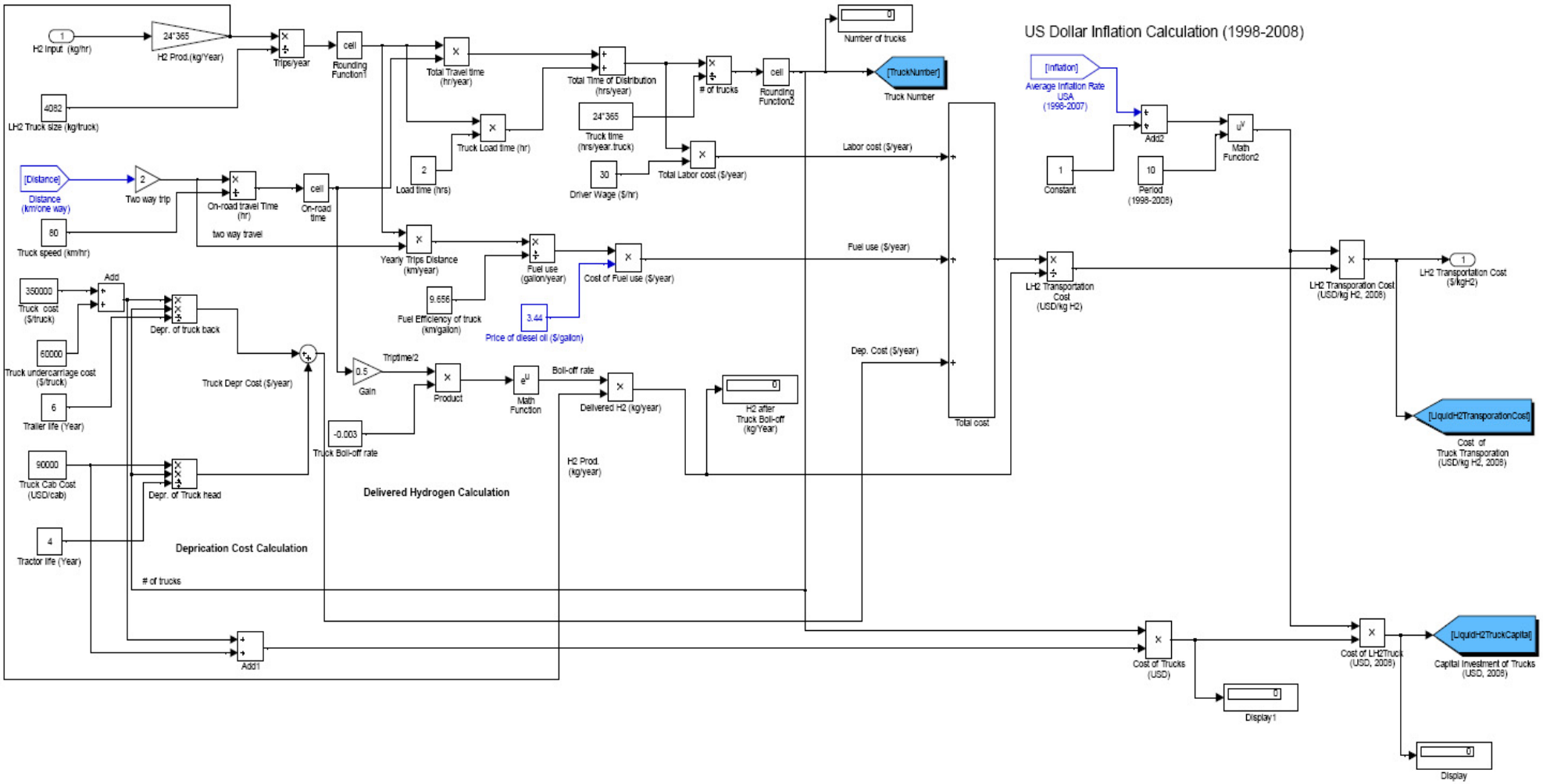
A16: Capital Investment of Liquid Hydrogen Storage Estimation Model



A17: Cost of Hydrogen Cryogenic Tanks Estimation Cost Model



A18: Operating Cost of Liquid Hydrogen Storage Estimation Model



A19: Total Cost of Liquid Hydrogen Truck Transportation Estimation Model

Appendix B
GMAS Codes of Heat Integration of S-I cycle Model

```
* The Heat Exchanger Network for S-I cycle

free variable number;
binary variables ys6,ys5,ys4,ys3,ys2,ys1,y71,y72,y73,y74,y75,y76,y21,y25,y11,
y15,y31,y35,y41;

positive variables
qc17,qc18,qc19,qc110,qc111,qc112,qc26,qc35,qc44,qc53,qc54,qc55,
qc56,qc57,qc58,qc59,qc510,qc61,qc62,qh18,qh19,qh110,qh111,qh112,qh113,qh27,qh28,
qh310,qh311,qh312,qh313,qh412,qh413,qh513,qh613,qh72,qh73,qh74,qh75,qh76,qh77,qh78,
qh79,qh710,qh711,qh712,qh713,qs61,rs1,qs62,q762,rs2,rh72,qs53,q753,rs3,rh73,qs44,qs54,
q744,q754,rs4,rh74,qs35,qs55,q735,q755,rs5,rh75,qs26,qs56,q726,q756,rs6,rh76,qs17,qs57,q217
,q257,q717,q757,rs7,rh77,rh27,qs18,qs58,q718,q758,q218,q258,q118,q158,rs8,rh78,rh28,rh18,qs
19,qs59,q719,q759,q119,q159,q219,q259,rs9,rh79,rh19,rh29,qs110,qs510,q7110,q7510,q1110,q1
510,q2110,q2510,q3110,q3510,rs10,rh710,rh110,rh210,rh310,qs111,q7111,q1111,q2111,q3111,rs
11,rh711,rh111,rh211,rh311,q2112,qs112,q7112,q1112,q3112,q4112,qh,cw;

equations
obj,c1,c2,c3,c4,c5,c6,c7,c8,c9,c10,c11,c12,c13,c14,c15,c16,c17,c18,c19,c20,
c21,c22,c23,c24,c25,c26,c27,c28,c29,c30,c31,c32,c33,c34,c35,c36,c37,c38,c39,c40,c41,c42,
c42,c43,c44,c45,c46,c47,c48,c49,c50,c51,c52,c53,c54,c55,c56,c57,c58,c59,c60,c61,c62,c63,
c64,c65,c66,c67,c68,c69,c70,c71,c72,c73,c74,c75,c76,c77,c78,c79,c80,c81,c82,c83,c84,c85,
c86,c87,c88,c89,c90,c91,c92,c93,c94,c95,c96,c97,c98,c99,c100,c101,c102,c103,c104,c105,c106,
c107,c108,c109,c110,c111,c112,c113,c114,c115,c116,c117,c118,c119,c120,c121,c122,c123,c124;

obj..
ys6+ys5+ys4+ys3+ys2+ys1+y71+y72+y73+y74+y75+y76+y21+y25+y11+y15+y31+y35+y41=e
=number;
c1..
qs61+rs1=e=qh;
c2..
qs61=e=qc61;
c3..
qs62+q762=e=qc62;
c4..
qs62+rs2=e=rs1;
c5..
rh72+q762=e=qh72;
c6..
qs53+q753=e=qc53;
c7..
qs53+rs3=e=rs2;
c8..
```

q753+rh73=e=rh72+qh73;
c9..
qs44+q744=e=qc44;
c10..
qs54+q754=e=qc54;
c11..
qs44+qs54+rs4=e=rs3;
c12..
q744+q754+rh74=e=qh74+rh73;
c13..
qs35+q735=e=qc35;
c14..
qs55+q755=e=qc55;
c15..
qs35+qs55+rs5=e=rs4;
c16..
q735+q755+rh75=e=rh74+qh75;
c17..
qs26+q726=e=qc26;
c18..
qs56+q756=e=qc56;
c19..
qs26+qs56+rs6=e=rs5;
c20..
rh76+q726+q756=e=qh76+rh75;
c21..
qs17+q217+q717=e=qc17;
c22..
qs57+q757+q257=e=qc57;
c23..
qs17+qs57+rs7=e=rs6;
c24..
q217+q257+rh27=e=qh27;
c25..
rh76+qh77=e=q717+q757+rh77;
c26..
qs18+q118+q218+q718=e=qc18;
c27..
qs58+q258+q758+q158=e=qc58;
c28..
qs18+qs58+rs8=e=rs7;
c29..
q118+q158+rh18=e=qh18;
c30..
rh27+qh28=e=q218+q258+rh28;
c31..

rh77+qh78=e=q718+q758+rh78;
c32..
qs19+q119+q219+q719=e=qc19;
c33..
qs59+q159+q259+q759=e=qc59;
c34..
qs19+qs59+rs9=e=rs8;
c35..
rh78+qh79=e=q719+q759+rh79;
c36..
q219+q259+rh29=e=rh28;
c37..
rh18+qh19=e=q119+q159+rh19;
c38..
q1110+qs110+q2110+q3110+q7110=e=qc110;
c39..
qs510+q1510+q2510+q3510+q7510=e=qc510;
c40..
qs110+qs510+rs10=e=rs9;
c41..
rh19+qh110=e=q1110+q1510+rh110;
c42..
q2110+q2510+rh210=e=rh29;
c43..
q3110+q3510+rh310=e=qh310;
c44..
rh79+qh710=e=q7110+q7510+rh710;
c45..
qs111+q1111+q2111+q3111+q7111=e=qc111;
c46..
qs111+rs11=e=rs10;
c47..
rh710+qh711=e=q7111+rh711;
c48..
rh110+qh111=e=q1111+rh111;
c49..
q2111+rh211=e=rh210;
c50..
rh310+qh311=e=q3111+rh311;
c51..
qs112+q1112+q3112+q4112+q7112+q2112=e=qc112;
c52..
qs112=e=rs11;
c53..
rh111+qh112=e=q1112;
c54..

rh211=e=q2112;
c55..
rh311+qh312=e=q3112;
c56..
q4112=e=qh412;
c57..
rh711+qh712=e=q7112;
c58..
qh113+qh313+qh413+qh513+qh713+qh613=e=cw;
c59..
qc61=e=23.5356;
c60..
qc62=e=154.923;
c61..
qc53=e=146.85;
c62..
qc54=e=12.502;
c63..
qc55=e=11.5404;
c64..
qc56=e=15.387;
c65..
qc57=e=20.965;
c66..
qc58=e=38.660;
c67..
qc59=e=17.599;
c68..
qc510=e=35.39;
c69..
qc44=e=27.782;
c70..
qc35=e=29.009;
c71..
qc26=e=46.387;
c124..
qc17=e=20.17;
c72..
qc18=e=37.197;
c73..
qc19=e=16.933;
c74..
qc110=e=34.051;
c75..
qc111=e=8.3277;
c76..

qc112=e=76.865;
c77..
qh18=e=5.09736;
c78..
qh19=e=2.32044;
c123..
qh110=e=4.662;
c79..
qh111=e=1.1412;
c80..
qh112=e=10.6766;
c81..
qh113=e=5.034;
c82..
qh27=e=15.9668;
c83..
qh28=e=28.1521;
c84..
qh312=e=7.3624;
c85..
qh311=e=0.7869;
c86..
qh310=e=3.2178;
c87..
qh313=e=3.4714;
c88..
qh412=e=13.4888;
c89..
qh413=e=6.36;
c90..
qh513=e=6.231;
c91..
qh613=e=25.73;
c92..
qh72=e=105.7413;
c93..
qh73=e=61.3243;
c94..
qh74=e=5.2208;
c95..
qh75=e=8.8352;
c96..
qh76=e=2.008;
c97..
qh77=e=9.1565;
c98..

qh78=e=16.144;
c99..
qh79=e=7.3493;
c100..
qh710=e=14.77888;
c101..
qh711=e=3.6144;
c102..
qh712=e=33.8147;
c103..
qh713=e=15.9435;
c104..
qs61+qs62-1000*ys6=l=0;
c105..
qs53+qs54+qs55+qs56+qs57+qs58+qs59+qs510-1000*ys5=l=0;
c106..
qs44-1000*ys4=l=0;
c107..
qs35-1000*ys3=l=0;
c108..
qs26-1000*ys2=l=0;
c109..
qs17+qs18+qs19+qs110+qs111+qs112-1000*ys1=l=0;
c110..
q762-1000*y76=l=0;
c111..
q753+q754+q756+q757+q758+q759+q7510-1000*y75=l=0;
c112..
q744-1000*y74=l=0;
c113..
q735-1000*y73=l=0;
c114..
q726-1000*y72=l=0;
c115..
q717+q718+q719+q7110+q7111+q7112-1000*y71=l=0;
c116..
q217+q218+q219+q2110+q2111+q2112-1000*y21=l=0;
c117..
q257+q258+q259+q2510-1000*y25=l=0;
c118..
q118+q119+q1110+q1111+q1112-1000*y11=l=0;
c119..
q158+q159+q1510-1000*y15=l=0;
c120..
q3110+q3111+q3112-1000*y31=l=0;
c121..

```
q3510-1000*y35=l=0;
c122..
q4112-1000*y41=l=0;


model problem/all/;
solve problem using mip minimizing number;
```